ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

Number 11

November 1958

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

SCIENTIST - TRANSLATORS WANTED

For over a decade, Consultants Bureau, Inc. has provided Western scientists with high quality cover-to-cover translations of Soviet scientific journals. Our unique contracts with the Soviet government are constantly revised to include more extensive coverage of technical activity in the USSR. In order to produce these journals at the high standards set down by both the Soviet and American governments, it is of prime importance to maintain a large staff of scientist-translators who can translate with precision in their specific scientific field. It is our strict policy to assign a translator only that material which is within his scope.

As part of our current and future* expansion programs, we have openings for a limited number of scientist-translators who can translate in the fields covered by the following journals:

Journal of General Chemistry

Antibiotics
Biochemistry
Bulletin of Experimental Biology and Medicine
Entomological Review
Microbiology
Pharmacology and Toxicology
Plant Physiology

Automation and Remote Control
Industrial Laboratory
Instruments and Experimental Techniques
Measurement Techniques

Czechoslovak Journal of Physics
Soviet Journal of Atomic Energy
Soviet Physics - Acoustics
Soviet Physics - Crystallography
Soviet Physics - Technical Physics

Our basic requirements are that the scientist-translator have a native command of English, a minimum degree of B.S. in his specific field, and a thorough knowledge of the contemporary technical terminology of his scientific discipline.

Translation may be done at home on a full or part-time basis.

For further information, please contact:

Translation Editor
CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, New York

*We expect, in the near future, to initiate a program of translation from the growing amount of important Chinese scientific literature available. In preparation, we are accepting applications from Chinese to English translators.

Number 11

November 1958

BULLETIN OF THE ACADEMY OF SCIENCES

OF THE USSR

Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
No. 1 *Jan.-Feb. 1952*

	U. S. and Canada	*Foreign*
Annual subscription	*$45.00*	*$50.00*
Annual subscription for libraries of non-profit academic institutions	*15.00*	*20.00*
Single issue	*5.00*	*5.00*

Copyright 1959
CONSULTANTS BUREAU INC.

227 W. 17th ST., NEW YORK 11, N. Y.

Editorial Board
(IZVESTIIA AKADEMII NAUK SSSR,
OTDELENIE KHIMICHESKIKH NAUK)

M. M. Dubinin (Editor-in-Chief), A. F. Kapustinskii (Acting Editor),
V. N. Kondrat'ev, A. N. Nesmeianov, K. T. Poroshin (Secretary)
I. I. Cherniaev

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners.

Printed in the United States of America

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

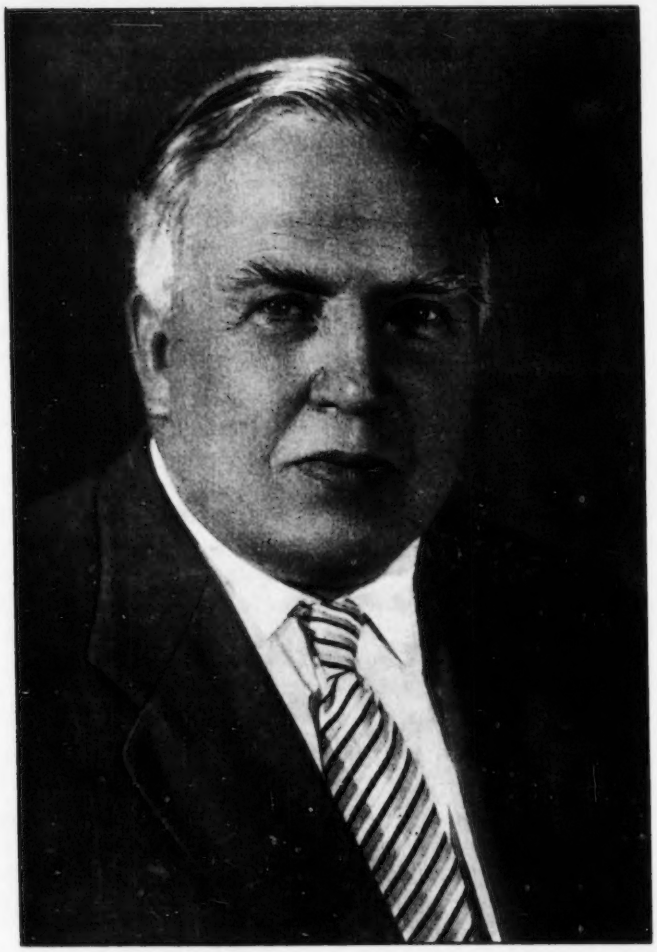
1958, Number 11 November

CONTENTS

	PAGE	RUSS. PAGE
Salute to P. A. Rebinder	1241	
The Main Tasks of Chemistry	1242	1285
Systems Containing Hydrogen Peroxide at High Concentration. Communication 15. The 10° Solubility Isotherm of the Ternary System $Ca(OH)_2-H_2O_2-H_2O$ and Further Characterization of the Solid Phases. S. Z. Makarov and N. K. Grigor'eva	1245	1289
The Effect of Radioactive Radiation on the Physical Chemical Properties of Solid Bodies. V. I. Spitsyn	1251	1296
The Dehydrogenation of Certain Hydroaromatic Hydrocarbons on a Chromate Catalyst. A. A. Balandin and G. V. Isaguliants	1257	1303
Overvoltage in the Electrodeposition of Antimony. A. P. Popkov, V. M. Gevorkian and A. T. Vagramian	1264	1310
Synthesis of Organomercury Compounds from Hydrazones. Communication 1. Reaction of Hydrazones of Aliphatic Aldehydes and Ketones with Mercuric Acetate. A. N. Nesmeianov, O. A. Reutov, A. S. Loseva and M. Ia. Khorlina	1269	1315
The Problem of the Stereochemistry of the Reaction of Symmetrical Organomercury Compounds with Mercuric Halides. A. N. Nesmeianov, O. A. Reutov, Wu Yang-Ch'ieh and Lu Ching-Chu	1280	1327
Esters of Phosphoric and Thiophosphoric Acids Containing Heterocyclic Radicals. Communication 1. Compounds with Pyrimidyl and Imidomethyluracil Radicals. A. Arbuzov and V. M. Zoroastrova	1284	1331
The Synthesis of Some Esters of α-(Dialkylphosphonyl)-β,β,β-trichloroethylphosphoric Acids and α-(Dialkylphosphonyl)-β,β,β-trichloroethyl Esters of Carboxylic Acids and Their Derivatives. K. V. Nikonorov.	1292	1340
Reactions of Fluoroolefins. Communication 8. Reactions of Perfluorovinylmagnesium Halides. I. L. Knuniants, R. N. Sterlin, R. D. Iatsenko and L. N. Pinkina	1297	1345
α,β-Disubstituted α-Acylaminocarboxylic Acids. Communication 2. A new Method of Preparing Oxazole-4-carboxylic Acids. O. V. Kil'disheva, M. G. Lin'kova, V. M. Savosina and I. L. Knuniants	1300	1348
Acetylene Derivatives. Communication 191. Preparation of Acids from Tertiary Acetylenic Alcohols. I. N. Nazarov, L. D. Bergel'son and V. I. Gunar	1306	1354
Transformations of Molecules in an Aqueous Medium. Krishna Bahadur and S. Ranganayaki.	1313	1361
Synthesis and Properties of α-Cyanoisopropoxysilanes and α-Cyanoisopropoxychlorosilanes. Communication 2. A. D. Petrov and V. M. Vdovin.	1317	1366

CONTENTS (continued)

	PAGE	RUSS. PAGE
Reaction of Trimethylsilylmethylmagnesium Chloride with Esters. E. V. Kukharskaya, D. N. Andreev and V. A. Kolesova	1323	1372
Isolation of Higher n-Alkanes from the 190-350° Fraction of Sokolovogorsk and Mirzaan Petroleums. N. G. Bekauri, N. I. Shuikin, Iu. P. Egorov and T. S. Shakarashvili	1327	1376
Carbon-Chain Polymers and Copolymers. 5. Copolymerization of Acrylonitrile and Methyl Methacrylate in the Presence of Tributylborine. G. S. Kolesnikov and N. V. Klimentova	1334	1383
Brief Communications		
The Synthesis of Nitromethane Labeled with Radiocarbon. P. I. Levin	1339	1388
Raman Spectrum Investigation of the Conformations of Cis- and Trans-1-acetyl-2-methyl-cyclohexanols. M. I. Batuev, A. A. Akhrem, A. D. Matveeva and I. N. Nazarov	1341	1389
The Raman Spectrum of Hexachlorobutadiene. M. I. Batuev and A. D. Matveeva	1344	1393
Reactions of Trialkyl Phosphites with Nitrosyl and Nitryl Chlorides. B. A. Arbuzov and E. N. Ukhvatova	1347	1395
Preparation of Organosilicon Ketones by the Dry Distillation of Salts of Organosilicon Acids. D. N. Andreev and E. V. Kukharskaia	1349	1397
Reaction of Trialkyl Phosphites with Phosgene. M. I. Kabachnik and P. A. Rossiiskaia	1350	1398
Current Events		
General Meeting of the Division of Chemical Science of the Academy of Sciences USSR. May 22-23, 1958	1351	1399
Symposium on the Organic and Nonsilicate Chemistry of Silicon. Dresden, May 12-14, 1958	1353	1401



Petr Aleksandrovich Rebinder

Highly esteemed Petr Aleksandrovich:

The Division of Chemical Science of the Academy of Sciences USSR and the Editorial Staff of the "Bull. Acad. Sci. USSR, Div. Chem. Sci." send you their sincere greetings on your sixtieth birthday and thirty-fifth year of scientific activity.

Your research in the field of physical chemistry of surface phenomena and modern colloid chemistry now constitutes a new scientific field – physicochemical mechanics, which is the scientific basis of a series of important branches in industry.

Dear Petr Aleksandrovich, we wish you good health and many years of productive scientific activity.

Division of Chemical Science of the Academy of Sciences USSR and the Editorial Staff of the "Bulletin of the Academy of Sciences USSR, Division of Chemical Science."

THE MAIN TASKS OF CHEMISTRY

The May Plenum of the Central Committee of the Communist Party of the Soviet Union heard and discussed a report delivered by the First Secretary of the Central Committee of CPSU, Chairman of the Council of Ministers USSR, Comrade N. S. Khrushchev, "On accelerating the expansion of chemical industry and in particular manufacture of synthetic materials and synthetic goods needed to satisfy the requirements of the people and the national economy."

The decision of the Plenum of the CC of CPSU* anticipated increased production of the more important chemical materials in 1959-1965 by not less than 2-3 times, a 4.5-8 fold increase in the manufacture of artificial and synthetic fibers, and plastics. The Plenum of the CC of CPSU noted that a successful fulfillment of the proposed goal is very important for continuing the technical progress in all the branches of national economy, for developing industrial power, for more efficient use of the nation's natural resources, so as to fully satisfy people's needs in textiles, clothes, shoes, and other widely needed goods. To solve this problem during the next Seven Year Plan (1959-1965) the following are anticipated: essential capital investment in chemical industry, full and varied utilization of chemical raw materials, in particular natural and recovered gases, gases from oil using plants, coal tar chemistry products, as well as a development of chemical processing of lumber industry products and agricultural waste products. There has to be a sharp increase in the output of modern equipment, machinery, instruments and means of automation, which the chemical industry badly needs; for this we anticipate a full use of currently active machine-building concerns as well as an accelerated construction of new specialized machine-construction plants.

A special place in the decisions of the Plenum of the CC of CPSU was devoted to problems of organizing scientific research work in the chemistry and physics of polymers and problems involving development and assimilation of commercial operations involved in preparing and processing synthetic products and other products which are now assuming a decisive importance.

To achieve the proposed goals we should accelerate the development of theoretical research in a series of chemical fields, and it is necessary to enlarge the experimental work on the preparation of new polymers. Despite a highly developed general level of chemistry in the USSR, there are some serious gaps in certain branches of it, particularly in the field of artificial and synthetic fibers and plastics. When analyzed, the causes of this lag turned out to have roots in a serious lack of organized scientific research and experimental work, in improperly rationed spending of hundreds of millions of rubles which are allocated yearly for these purposes, and in scattered facilities over many and often nonessential projects. Besides, certain scientific institutes and scientists are out of touch with industrial problems and for years do not contribute anything to the country, while individual scientific workers spend endless hours on old projects without participating in the search for new scientific methods. The effectiveness of work done at research institutes is also decreased by poor coordination in their activities and duplication in various subjects, which results in an inefficient use of specialists and breeds irresponsibility.

The Academy of Sciences USSR, the scientific academies of other Soviet republics, and our country's colleges did not devote enough time to the solution of scientific problems connected with the manufacture and applications of synthetic materials.

What are the basic problems facing Soviet chemists? First of all, we have to consider that the most urgent matter is the development of prospecting and theoretical projects in the field of polymers and starting materials in order to assume a leading role in the world in this field. Great tasks are also facing the professional scientific

*Central Committee of the Communist Party of the Soviet Union.

research institutes engaged in polymer work and their mainstays – factory laboratories. The complexity of these problems places new demands on the scientists in various fields, from theoretical physics to chemistry and biology. For the purpose of organizing all these efforts on an All-Union scale, a Scientific Committee on Polymers has been created at the Division of Chemical Science Acad. Sci. USSR. It will direct and coordinate scientific work and assist in realizing practical and theoretical progress in this field.

In his talk at the June 1958 session of the Academy of Sciences USSR, Academician A. N. Nesmeianov, president of the Academy of Sciences USSR, having described the more important synthetic products, ways of preparing them, and their structural peculiarities, noted the diversity and complexity of fundamental problems, which impose on Soviet science a demand for speedier development of work in the field of high-polymer compounds. This field is somewhat bigger than just a division of organic chemistry or chemistry in general. It is a new phase in the development of a whole group of sciences, mainly chemistry, physics, biochemistry, and biology, and requires the introduction of new scientific concepts and experimental methods. The creation of new materials and the need for wider practical utilization of them demand some cooperation between scientists and engineers in the most diverse departments. In the work on the synthesis of high-molecular compounds it is necessary to start from general methods of low-molecular organic chemistry, to study more profoundly biosynthetic methods, and to develop inorganic and heteroorganic high-molecular chemistry.

In the development of high-molecular chemistry an exceptionally important part will be played by physical research, the principal work of which should aim at establishing a connection between the molecular structure and the properties of polymers. A particularly important task in connection with this is the study of the relative distribution of chain molecules in the bulk of the polymeric material. To determine the connections between the structure of chain molecules, types of molecular packing and a whole set of mechanical properties, we will have to carry out a wide investigation of the latter. Moreover, the mechanical properties of polymers and things made from them should be determined and evaluated by completely new methods. Without this a wide assimilation of new materials by technology will not be possible.

One of the most important problems connected with the preparation of high-quality fibers and anisotropic films is that of molecular orientation in polymers, and since the intermediate steps in the conversion of polymers to various goods (fibers, films, etc.) involve solutions, then the investigation of the latter will be of essential importance. Data will have to be obtained on the distribution of molecules according to molecular weight, shape, and dimension of individual polymeric molecules; it will be necessary in turn to establish the dependence of shape and dimensions of polymeric molecules on their internal structure and interaction with the solvent. One should apply the most recent physical methods of structural analysis and in this manner work out means of determining molecular distribution functions in the polymer according to various characteristic structural irregularities, types of branching, sequence of individual links in the chain, etc. The problem of creating the foundations for a theory of the processing and formation of polymers also has to be solved so that we may utilize mechanicochemical properties for preserving and improving the properties of polymers in the processing stage. A large number of other tasks confront science in connection with the solution of problems involved in high-polymer compounds.

In order to extend considerably the volume of scientific research work in this field and to shorten the time required for it we plan to expand hundreds of scientific establishments in 1958-1960. At the same time certain colleges will have to be expanded, and new ones formed to train specialists in the polymer industry. A series of institutes at the Academy of Sciences USSR will be expanded. New institutes will be set up. At the Institute of Heteroorganic Compounds of the Acad. Sci. USSR a new section will be organized whose work will primarily be directed toward utilizing heteroorganic (organosilicon, organophosphorus, et al.) and inorganic monomers in the synthesis of polymers. At the same Institute work will be carried out to develop a theoretical foundation for high-polymer chemistry and synthesize new types of fibrous polymers. The new sections formed at the Institute of High-Polymer Compounds will take over projects in the field of synthesis of new polymers, copolymers and block polymers and also problems connected with the investigation of physicochemical properties of polymers, kinetics of catalytic polymerization, destruction and stabilization of polymers. The laboratories being set up at the Institute of Chemical Physics will help develop the work on polymerization kinetics, kinetics of oxidation processes which occur during the reprocessing of hydrocarbons, and also help work out the theoretical bases for the preparation of block polymers and graph polymers, the physics and physical chemistry of reinforced plastics, etc. The Institute of Physical Chemistry will be assigned the job of developing the scientific bases for the application of polymers to construction work, agriculture (to improve the texture of soil), and other purposes. New laboratories are being

set up for this. Besides, this Institute will have to intensify the work on the catalytic synthesis of monomers, macrokinetics of catalytic processes, use of radiation in polymerization and vulcanization, and carry out a series of other projects which fall within its framework. Work on the synthesis of monomers by the use of catalytic processes and irradiation will be developed at the Institute of Organic Chemistry. Problems connected with the utilization of petroleum and natural and recovered gases in the preparation of polymeric materials will be worked out at the newly created Institute of Petrochemical Synthesis in Moscow, which is affiliated with the Petroleum Institute of the Acad. Sci. USSR. The following are being formed in outlying areas: Institute of Organic Chemistry of the Acad. Sci. USSR in Kazan — the scientific center for petroleum chemistry in the petroleum districts of Second Baku; Institutes of Organic Chemistry in Novosibirsk and Irkutsk (as a part of the Novosibirsk Section of the Acad. Sci. USSR) — theoretical scientific centers for the Eastern districts of the Nation concerned with the problems of petrochemical synthesis and polymer chemistry. The Institute of Catalysis which is being formed in Novosibirsk will remain in close contact with them. Of great importance to the progress of chemical science will be a continuing and diversified development in the field of natural products, and of primary importance in the chemistry of albumin. In connection with this, the Institute of Natural Products of the Acad. Sci. USSR is being formed; it will be primarily concerned with the structure of albumin, polysaccharides, and cellulose, and the synthesis of biologically active substances. To coordinate all this work a committee on the chemistry of natural products was set up at the Division of Chemical Science of the Acad. Sci. USSR.

By working according to the same plan as the scientific institutes of the Acad. Sci. USSR, different industrial scientific establishments should considerably strengthen their cadres, material and technical foundations, create modern experimental stations designed on a high technical level, and participate in the organization of experimental plants and factories.

An exceptional responsibility in organizing the action for the advancement of Chemistry is facing Soviet scientists-chemists. The Extraordinary XXI Congress of the Communist Party of the Soviet Union will examine the actual figures for the development of the national economy of USSR in the years 1959-1965, in which the advancement in the chemical science and industry will be defined according to the decisions arrived at at the May Plenum of the CC of CPSU.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION

COMMUNICATION 15. THE 10° SOLUBILITY ISOTHERM OF THE TERNARY SYSTEM $Ca(OH)_2-H_2O_2-H_2O$ AND FURTHER CHARACTERIZATION OF THE SOLID PHASES

S. Z. Makarov and N. K. Grigor'eva

The ternary $Ca(OH)_2-H_2O_2-H_2O$ system has previously been studied [1] in the 0 to −21° range by the solubility method. It was established and proved conclusively that the reaction between a calcium hydroxide solution and hydrogen peroxide gave rise to solid phases of a peroxide nature: calcium peroxide hydrates $CaO_2 \cdot 8H_2O$ and $CaO_2 \cdot 2H_2O$, and a diperoxyhydrate of calcium peroxide – $CaO_2 \cdot 2H_2O_2$. Thermal analysis confirmed [2] the fact that all the solid phases were actually individual calcium peroxide compounds, and established the stability range of each phase. Solubility isotherms [1] showed the regions in which the phases existed and the conditions of formation as a function of temperature and hydrogen peroxide concentration in solution.

10° Isotherm

At 10° the $Ca(OH)_2-H_2O_2-H_2O$ system was investigated from very low to 93% concentrations of hydrogen peroxide. Experimental results are compiled in Table 1 and graphically represented on a triangular phase diagram in Fig. 1. At 10° the region of calcium peroxide octahydrate almost completely disappears. $CaO_2 \cdot 8H_2O$ can be detected only if the H_2O_2 concentration in the liquid phase does not exceed 0.10%. There were basically only two phases, $CaO_2 \cdot 2H_2O$ in the 0.10 to 22.0% H_2O_2 concentration range and $CaO_2 \cdot 2H_2O_2$ in the 22.0 to 78.5% concentration range; the last one is the limiting value since strong decomposition of H_2O_2 in solution is observed above it.

TABLE 1

10° Isotherm of the $Ca(OH)_2-H_2O_2-H_2O$ System

No. of points	Initial H_2O_2 conc., based on		Liq. phase comp. in %				Comp. of residues in %			Comp. of solid phases
	H_2O_2	Act. O_2	Act.O_2	CaO	H_2O	H_2O_2	Act.O_2	CaO	H_2O	
1	5,40	2,54	0,05	0,10	99,85	0,106	6,82	27,00	66,18	$CaO_2 \cdot 8H_2O$
22	8,11	3,81	0,76	0,064	99,18	1,61	13,12	40,07	46,81	$CaO_2 \cdot 2H_2O$
12	10,0	4,70	2,15	0,07	97,78	4,57	11,85	38,70	49,45	Ditto
11	12,2	5,73	2,65	0,075	97,28	5,64	12,05	30,6	57,89	"
3	16,0	7,52	3,50	0,11	96,39	7,44	11,40	31,50	57,10	"
20	20,0	9,40	5,36	0,18	94,46	11,40	14,33	37,61	48,06	"
21	22,0	10,34	6,20	0,22	93,62	13,19	14,65	40,80	44,55	"
16	31,0	14,57	7,80	0,31	91,89	16,60	15,56	36,22	48,22	"
15	36,0	16,92	9,81	0,36	89,83	20,87	18,05	35,72	46,23	"
2	28,5	13,40	9,85	0,28	89,87	20,95	14,35	35,05	50,60	
23	37,0	17,40	10,22	0,22	89,56	21,74	31,14	33,93	34,93	$CaO_2 \cdot 2H_2O_2$
24	44,6	20,96	12,80	0,26	86,94	27,23	27,38	28,98	43,64	Ditto
13	52,0	24,44	17,85	0,33	81,82	38,00	28,75	27,38	43,87	"
9	84,0	39,48	29,00	0,32	70,68	61,70	32,83	26,83	40,34	"
10	93,0	43,71	36,90	0,11	62,99	78,51	35,10	23,70	41,20	"

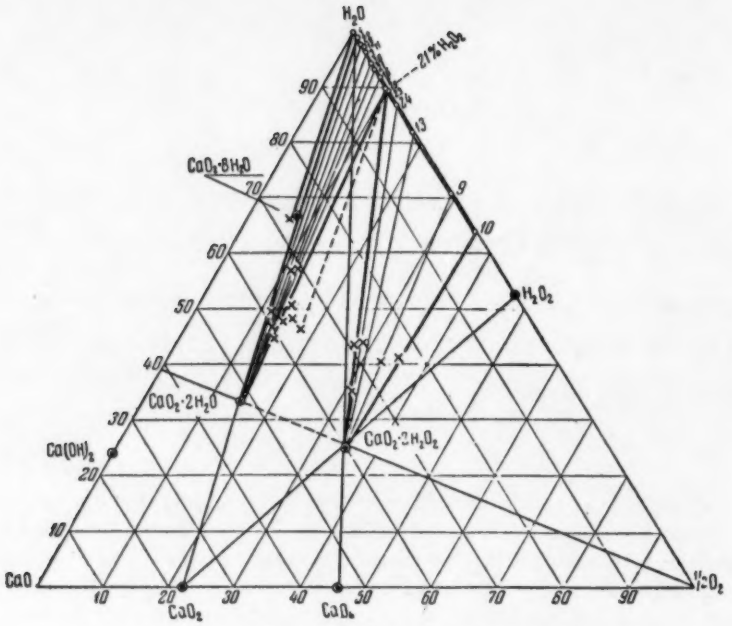


Fig. 1. 10° Isotherm of the $Ca(OH)_2-H_2O_2-H_2O$ system.

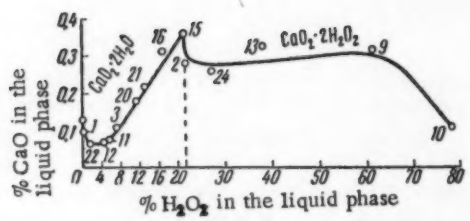


Fig. 2. 10° Isotherm of the $Ca(OH)_2-H_2O_2-H_2O$ system.

In Fig. 2, the solubility of solid CaO (in %) is plotted in rectangular coordinates as a function of the H_2O_2 contents in the liquid phase. Inspection of the data shows that at 10° the graph contains two solubility branches, one corresponding to $CaO_2 \cdot 2H_2O_2$, the other to $CaO_2 \cdot 2H_2O$. The solubility of $CaO_2 \cdot 2H_2O$ increases considerably with increase in H_2O_2 concentration, whereas $CaO_2 \cdot 2H_2O_2$ concentration ranges from 0.22 to 0.32% while above 60% the H_2O_2 content drops off sharply.

Polythermal Diagram

On the basis of isothermal solubility data (Table 2) we constructed a polythermal diagram (Fig. 3) for the $Ca(OH)_2-H_2O_2-H_2O$ ternary system in the −21° to +10° temperature range. Calcium peroxide diperoxyhydrate occupies the largest area. At low H_2O_2 concentrations in the −10 to +10° range this area borders on that of calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$, while from −10° to −21° it is in direct contact with that of $CaO_2 \cdot 8H_2O$. At high H_2O_2 concentrations (in the liquid phase) the $CaO_2 \cdot 2H_2O_2$ area between −21° and 0° is bound by that of solid hydrogen peroxide, while at higher temperatures it is limited by the stability of hydrogen peroxide in solution.

Calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$ forms above −10° and with rise in temperature its surface widens appreciably attaining a 22% concentration of hydrogen peroxide at +10°. Calcium peroxide octahydrate exists over the whole temperature range investigated. However, it has varying stability regions. Thus, at −21° the region is very narrow and $CaO_2 \cdot 8H_2O$ exists at a rather high H_2O_2 content in the liquid phase, 24.5-28%. This becomes fully understandable if we remember that below −21° solutions containing less then 24% of H_2O_2 freeze. When the temperature is raised from −21 to −10° the $CaO_2 \cdot 8H_2O$ region becomes slightly wider (14.8-21.8%) and shifts toward lower concentrations giving way to $CaO_2 \cdot 2H_2O$, which does not form below −10°. This region is also limited by the freezing of solutions. When the temperature is further raised to 0° the region of $CaO_2 \cdot 8H_2O$

TABLE 2

Boundaries of Crystallization Surfaces of the Solid Phases in the $Ca(OH)_2$–H_2O_2–H_2O Ternary System

Phases	% H_2O_2 conc. in the liq. phase (temp. in °C)			
	10	0	−10	−21
$CaO_2 \cdot 8H_2O$	0,0–0,10	0,0–6,0	14,8–21,8	24,5–28,0
$CaO_2 \cdot 2H_2O$	0,10–22,0	6,0–24,8	None	None
$CaO_2 \cdot 2H_2O_2$	22,0–78,5	24,8–88,0	21,8–91,0	28,0–82,0

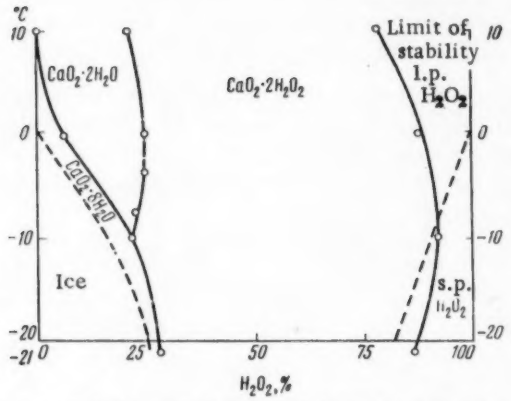


Fig. 3. Polythermal diagram of the $Ca(OH)_2$–H_2O_2–H_2O system.

stability shifts towards lower H_2O_2 concentrations (in the liquid phase), below 5-6%. When the temperature is raised to 10° the region $CaO_2 \cdot 8H_2O$ narrows down appreciably, to only 0.10% H_2O_2 (in the liquid phase) at 10°.

X-Ray Crystallographic Investigations and Microphotographs of the Solid Phases

To supplement previously described properties of the solid components of the system we carried out an x-ray crystallographic investigation of calcium peroxide compounds and also took some microphotographs of them. x-Ray powder photographs of these compounds* were taken in chambers 86.0 and 57.3 mm in diameter by using a copper radiation source and a nickel filter. Samples of CaO_2, $CaO_2 \cdot 2H_2O$, and $CaO_2 \cdot 8H_2O$ were placed in celluloid capillaries and photographed at room temperature. Samples of $CaO_2 \cdot 2H_2O_2$ were sealed off in pyrex capillaries and photographed at ~−45°. Low-temperature photography was carried out in a special chamber where the samples were placed in a stream of liquid nitrogen vapor.

Anhydrous Calcium Peroxide. The structure of CaO_2 was already investigated by Kotov and Raikhshtein [3], Neiding and Kazarnovskii [4], and by Reinhardt [5]. It was established that CaO_2 belongs to the tetragonal system with lattice parameters: a = 4.90 A, c = 5.94 A. A unit cell contains 4 molecules. Calcium atoms occupy the following positions in the lattice: 000, $\frac{1}{2}$ $\frac{1}{2}$ 0, $\frac{1}{2}$ 0 $\frac{1}{2}$, 0 $\frac{1}{2}$ $\frac{1}{2}$. The centers of mass of O_2 molecules occupy the following positions: 00 $\frac{1}{2}$, $\frac{1}{2}$ 00, 0 $\frac{1}{2}$ 0, $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$. A schematic representation of the atomic distribution in a CaO_2 lattice is shown in Fig. 4.

In Fig. 5, a, b, c, and d, we have drawn a schematic representation of x-ray powder patterns we obtained with CaO_2, $CaO_2 \cdot 2H_2O$, $CaO_2 \cdot 8H_2O$, and $CaO_2 \cdot 2H_2O_2$; the lines in the graph give interplanar distances in angstroms while their lengths give relative intensities of spectral lines. The data obtained with 92% CaO_2 (Fig. 5, a) is in good agreement with Reinhardt's data (which was obtained on samples containing 75% CaO_2).

Anhydrous calcium peroxide exists under ordinary conditions in the form of fine crystalline powder of a light-cream color (exact tone depends on the degree of dispersion). The crystal structure of CaO_2 can also be seen very distinctly under a microscope; CaO_2 crystals form crystalline aggregates which are anisotropic in polarized light, indicating that they belong to a lower symmetry group than cubic. x-Ray analysis indicates that they belong to the tetragonal system. The size of crystals obtained usually did not exceed 30-40 μ.

*Experiments were carried out at the Laboratory of Peroxide Compounds at the Institute of General and Inorganic Chemistry, Acad. Sci. USSR, under the direction of G. A. Gol'der.

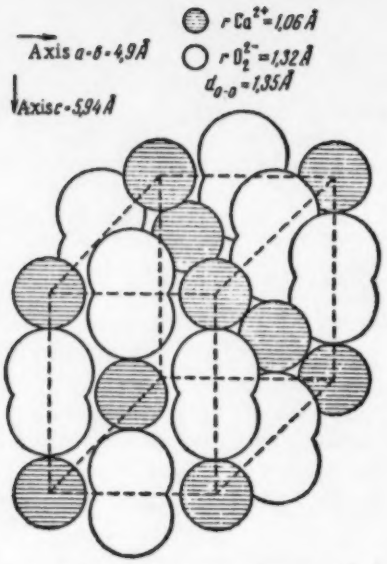


Fig. 4. Schematic representation of the atomic distribution in a CaO_2 crystal lattice.

Calcium peroxide dihydrate. The sample of $CaO_2 \cdot 2H_2O$ which was used in the x-ray study contained 91% of $CaO_2 \cdot 2H_2O$. Its x-ray powder patterns (which are schematically represented in Fig. 5, b) are similar to those of CaO_2; this fact permits the assumption that the introduction of two water molecules into the CaO_2 crystal lattice does not change the basic lattice structure.

The crystal structure of $CaO_2 \cdot 2H_2O$ can be seen much more clearly than that of anhydrous CaO_2. Magnification (×160) shows well-formed individual crystals 40 μ in size which are anisotropic and show less tendency toward aggregation. The degree of anisotropy is close to that of anhydrous CaO_2, and therefore, as far as the general form of these crystals is concerned (tetragonal appearance), one may assume that the symmetry of $CaO_2 \cdot 2H_2O$ crystals is not higher than tetragonal either. Crystal powders of $CaO_2 \cdot 2H_2O$ have a rusty color whose intensity increases with crystal size.

Calcium peroxide octahydrate. Shineman and King [6] studied the structure of calcium peroxide octahydrate; they established that $CaO_2 \cdot 8H_2O$ crystals belong to the tetragonal system and have lattice parameters: a = 6.21 A, c = 11.00 A.

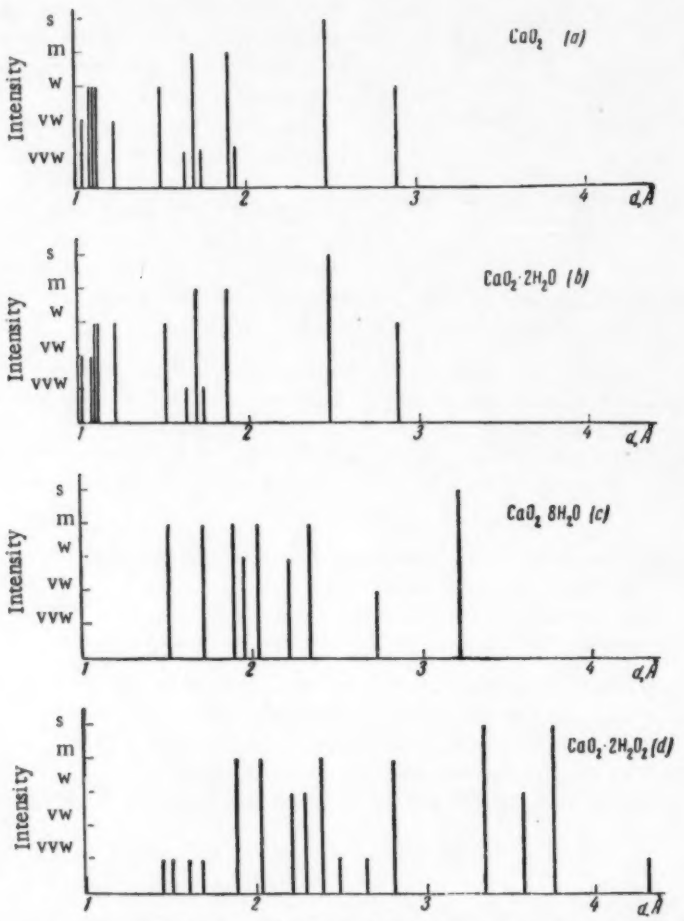


Fig. 5. Intensity diagram of principal lines in x-ray patterns of calcium peroxide compounds. s) strong; m) medium; w) weak; vw) very weak; vvw) very very weak.

A unit cell contains two molecules; the space group is D^8_{4h} —p 4/ncc. In accordance with the space group classification, calcium atoms occupy fourfold positions: 4 (a) and 4 (b), z = 0 or $\frac{1}{4}$. Oxygen molecules are located at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm w$, where w = 0.12, while water molecules occupy sixteenfold general positions with parameters x = 0.30, y = 0.11, z = 0.13. The sample of $CaO_2 \cdot 8H_2O$ used in our x-ray analysis contained 7.10 act. O_2 and 27.30% CaO. The x-ray pattern is schemetically represented in Fig. 5,c. Our data fully agreed with that of Shineman and King, who carried out their investigation on a single crystal.

Of all the calcium peroxide compounds $CaO_2 \cdot 8H_2O$ forms the best crystals; they are square, belong to the tetragonal system (Fig. 6) and show distinct anisotropy in polarized light. The crystal dimensions vary over a wide range of sizes, depending on the conditions of preparation, and may attain 230-240 μ. The separation of such large crystals from the mother liquor is easier and makes it possible to prepare highly pure compounds. In isolated cases we observed under the microscope crystals which were compressed in the middle of a face; this was evidently connected with the formation of complex overgrowths. $CaO_2 \cdot 8H_2O$ crystals are pearly-white and will remain quite unchanged for a long time if kept in tightly sealed containers at ordinary temperatures. They decompose in air. In the presence of dehydrating agents or when heated they readily lose their water of crystallization.

Fig. 6. A microphotograph of $CaO_2 \cdot 8H_2O$ crystals.

Calcium peroxide diperoxyhydrate. As was already said before, x-ray powder photographs of $CaO_2 \cdot 2H_2O_2$ were taken at a low temperature. The sample under investigation was pure calcium peroxide diperoxyhydrate with an admixture of water, $CaO_2 \cdot 2H_2O_2 \cdot 0.9H_2O$. The x-ray photograph is schematically represented in Fig. 5,d. x-Ray data show that the interplanar distances are very different from those of the above investigated compounds, which suggests a distinct structure for this compound. The determination of symmetry and the dimensions of a unit cell of this compound will require additional research. The crystal form of calcium peroxide diperoxyhydrate is similar to that of $CaO_2 \cdot 2H_2O$, except that the crystals are considerably less stable at ordinary temperatures. If $CaO_2 \cdot 2H_2O_2$ is examined in polarized light under a microscope, a distinct luminescence is observed when the Nicol prisms are crossed. The size of individual crystals usually does not exceed 30-40 μ. Unlike $CaO_2 \cdot 2H_2O$, $CaO_2 \cdot 2H_2O_2$ is not rust-colored but white, and when the hydrogen peroxide of crystallization is decomposed it changes to $CaO_2 \cdot 2H_2O$. This transformation is easily detected by the change in the color of crystals. $CaO_2 \cdot 2H_2O_2$ crystals can be stored for a long time only in hermetically sealed containers and at temperatures not above —10° to —20°C.

SUMMARY

1. From the isothermal solubility data between —21 and +10° we constructed a polythermal diagram of the $Ca(OH)_2-H_2O_2-H_2O$ ternary system with solid phases of $CaO_2 \cdot 8H_2O$, $CaO_2 \cdot 2H_2O$, and $CaO_2 \cdot 2H_2O_2$.

2. The crystals of anhydrous calcium peroxide, its hydrates and peroxyhydrates belong to a lower symmetry system than cubic.

3. An x-ray crystallographic investigation of CaO_2 and $CaO_2 \cdot 8H_2O$ powders supported the literature data which assigned to these crystals tetragonal symmetry.

4. Introduction of two water molecules into a CaO_2 lattice produces only an insignificant change in its basic structure. Evidently the water molecules occupy vacant places between the atoms.

5. The x-ray photographs of $CaO_2 \cdot 2H_2O_2$ powders differ very sharply from those of the other calcium compounds, which indicates that this compound possesses a distinct structure of its own.

N. S. Kurnakov
Institute of General and Inorganic
Chemistry, Acad. Sci. USSR

Received May 17, 1957

LITERATURE CITED

[1] S. Z. Makarov and N. K. Grigor'eva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 385.*

[2] S. Z. Makarov and N. K. Grigor'eva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 598.*

[3] V. Kotov and S. I. Raikhshtein, J. Phys. Chem. 15, 1057 (1941).

[4] A. B. Neiding and I. A. Kazarnovskii, J. Phys. Chem. 26, 1167 (1952).

[5] Reinhardt, x-Ray Crystallographic Studies of Peroxide Structures,* Div. Sov. State Akts. Society "Photofilm."

[6] R. Shinemann and A. King, Acta cryst. 4, 67 (1951).

*Original Russian pagination. See C. B. Translation.

THE EFFECT OF RADIOACTIVE RADIATION ON THE PHYSICAL CHEMICAL PROPERTIES OF SOLID BODIES

V. I. Spitsyn

Report at the General Session of the Division of Chemical Science of the Academy of Sciences of the USSR, May 22, 1958

Radioactive transformations, occurring in a solid body, can lead to various changes within this body and on its surface. It is known that radioactive preparations become electrically charged. Under the action of radiation a partial ionization of the atoms, or the passage of these atoms into an excited state, is to be observed. Nuclear recoil can produce crystal lattice defects in a solid body and lead to its structural disintegration; at the same time, additional active centers will be formed on the surface. For these reasons, radioactive irradiation of solid bodies should markedly affect such heterogeneous processes as adsorption, isotopic exchange, and catalytic activity. These effects have scarcely been dealt with in the existing literature. Certain authors have studied the results of external irradiation of solid bodies by γ-rays [1-3], neutrons [4], and positive ions [5]. By such procedures, it has been possible to increase the catalytic activity in certain cases. Conclusive results were not obtained in earlier work on the irradiation of catalysts with x-rays [6].

The author and his co-workers have investigated the radioactive irradiation of solid bodies and its effect on isotopic exchange and adsorption, and on other processes occurring in heterogeneous systems involving these materials.* Spitsyn and Mikhailenko have studied the relation between the intensity of the β-radiation from sulfur-35, and the degree of isotopic exchange of sulfur between solid potassium sulfate, tagged with S^{35}, and gaseous sulfuric anhydride. These investigations were carried out at 840° under fixed conditions, using preparations of K_2SO_4 of various specific activities. A sketch of the apparatus is given in Fig. 1.

Dry air was passed through the apparatus prior to, and after, each experiment. The temperature was held constant to within ±5°. In each experiment, the charge of the sulfate was 0.3-0.4 g and the amount of SO_3, 0.3 ml. or 0.58 g. The flow rate of the dry air, with its included sulfuric anhydride, reached 37 liters/hr. The time of passage of the SO_3 over the preparation which was under study, was 10 minutes. The sulfate charge was held in the heated zone of the furnace for 20 minutes. Earlier work [7] had shown that the experimental conditions (840° temperature, 19.9 mm partial pressure of SO_3 in the incident gaseous mixture) were such that weighable quantities of pyrosulfates would not be formed. At the same time, the potassium sulfate did not reach the melting point, and was not subject to thermal dissociation.

Solutions of K_2SO_4 containing active sulfur were prepared by the introduction of small amounts of active sodium sulfate, this being the form in which S^{35} is customarily supplied. These solutions were then evaporated to dryness and the residues heated at 800°. Uniformity in the specific surfaces of the K_2SO_4 specimens was assured by subjecting the carefully pulverized preparations to a separation into fractions by screening through silk sieves. The particle dimensions varied from 0.10 to 0.17 mm.

On the completion of an experiment, the charge of active sulfate was dissolved in a measuring flask. A definite volume of this solution was then evaporated onto a sheet of filter paper which was held in a circular

*This work was carried out in conjunction with the Institute of Physical Chemistry of the Academy of Sciences of the USSR and the Chemistry Department of the M. V. Lomonosov State University in Moscow.

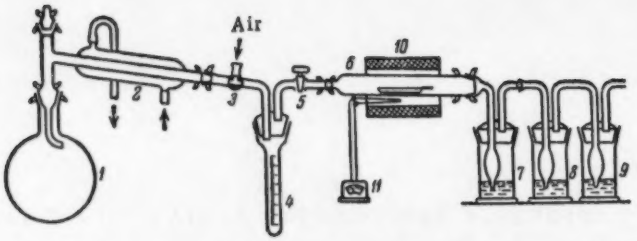


Fig. 1. Sketch of apparatus for studying the isotopic exchange of sulfur in the $K_2\overset{*}{S}O_4-SO_3$ system: 1) bulb for the distillation of SO_3; 2) condenser; 3, 5) stopcocks; 4) measuring tube for SO_3; 6) working tube and quartz boat; 7) scrubber (conc. H_2SO_4); 8-9) scrubbers (0.1 N NaOH); 10) furnace; 11) pyrometer.

TABLE 1

The Isotopic Exchange of Sulfur Between Potassium Sulfate and SO_3, at 840°

No. $K_2\overset{*}{S}O_4$ preparation	Added $Na_2\overset{*}{S}O_4$, in %	Observed specific activity, in counts/min·g	Absolute activity, in mC/g	Number of experiments	Mean degree of exchange, in %
1	0,04	$6,44\cdot10^5$	$1,7\cdot10^{-2}$	5	11,7
2	0,1	$9,37\cdot10^5$	$2,6\cdot10^{-2}$	6	11,5
3	0,1	$12,5\cdot10^6$	$3,5\cdot10^{-1}$	4	26,7
4	0,4	$72,6\cdot10^6$	2,0	5	65,5
5	0,4	$80,4\cdot10^6$	2,3	5	66,9
6	2,6	$28,2\cdot10^7$	7,8	5	33,3
7	3,0	$58,5\cdot10^7$	16,2	4	36,6

aluminum cup. The specimen activity was always measured under the same geometrical relations with respect to the end-window counter. The high activity solution which was obtained at the end of an experiment was so diluted that the impulse count would be approximately the same (1500-2000 counts/min) in each case. Four to six experiments of isotopic exchange were carried out on each preparation of given specific activity. The degree of exchange was calculated from the equation

$$W = (A_0 - A_1)\frac{1}{B},$$

in which W is the degree of exchange, in percent; A_0 is the activity of the original salt, considered to be 100%; A_1 is the activity of the reaction product, expressed as a percentage of the activity of the original compound; $B = N_1/(N_1 + N_2)$; N_1 is the atomic concentration of the element under study (sulfur) in the incident SO_3; and N_2 is the atomic concentration of sulfur in the radioactive preparation.

From the results which were obtained (Table 1), it follows that the rate of isotopic exchange was practically constant at 12% when the specific radioactivity of the $K_2\overset{*}{S}O_4$ was ~0.02-0.03 mC/g. The degree of exchange then rose with increasing activity of the potassium sulfate, reaching a maximum of ~67% at a specific activity of ~2 mC/g. Further increase of the specific activity of the potassium sulfate to 8-16 mC/g once more led to a decrease in the degree of exchange to 33-37%. The region of higher specific activities was not investigated.

In these experiments radiochemical breakdown of the potassium sulfate, such as would be accompanied by the splitting off of SO_3 and a corresponding drop in the activity, was not observed. An active preparation of $K_2\overset{*}{S}O_4$, heated in a current of air under the same conditions as in the exchange experiments with SO_3, showed absolutely no alteration either in weight, or in the content of S^{35}. Variation in the amount of added sodium sulfate (the carrier of S^{35}) was also totally without effect on the rate of isotopic exchange in the potassium sulfate. For a $K_2\overset{*}{S}O_4$ preparation which contained 0.4% Na_2SO_4 and had a specific activity of $1.7 \cdot 10^{-2}$ mC/g, the rate of isotopic exchange of 11.9% was practically identical with the rate of exchange (11.7%) at this same specific activity (preparation No. 1, Table 1), but with a lower Na_2SO_4 content (0.04%).

It was possible to suppose that the β-particles emitted by the S^{35} would give rise to an excitation of the ions forming the K_2SO_4 crystal lattice, and of the SO_4^{2-} ions, in particular, at sufficiently high radiation intensity. This would favor the process of isotopic exchange. It was also possible that a still more significant role would be played by those crystal lattice defects arising at points where radioactive disintegration had taken place. In any case, the number of sulfur atoms entering into isotopic exchange exceeded the observed number of acts of radioactive transformation in the course of an experiment by a factor of 10^{14}. The thought thus suggests itself that a large number of active centers must have appeared on the surface, and in the bulk of the solid body under the influence of its radioactivity.

It should be noted that the crystal lattice defects and possibly the effects of disintegration are retained in the potassium sulfate for long periods of time. Radioactive preparations of K_2SO_4 which were held until their activity had markedly diminished, still showed a high rate of isotopic exchange with SO_3, this rate being increased in comparison with the original value (Table 2) rather than diminished. This increase in the rate of exchange was the more marked, the higher the initial activity of the preparation and the longer the holding time.

TABLE 2

The Relation Between the Change in the Rate of Isotopic Exchange and the Holding Time of Radioactive Preparations

No. $K_2\overset{*}{S}O_4$ preparation	Holding time, in days	Specific activity, in mC/g		Degree of exchange of sulfur, in %	
		before holding	after holding	before holding	after holding
4 (Table 1)	93	2.0	0.85	65.5	69.4
7 (Table 1)	270	16.2	1.9	36.6	78.0

The reason for the appearance of an exchange maximum in potassium sulfate of ~2 mC/g specific activity (Fig. 2) is still unclear. It is possible that electrical charges rapidly develop on the surface of the solid potassium sulfate when the intensity of radioactive irradiation is too high and that these retard the absorption of molecular SO_3 out of the gaseous phase, thus impeding the exchange process. It can be, too, that ionization of the SO_3 molecules arises under the action of the radiation to lead to similar effects. In any case, our measurements on this system showed the energy of activation for isotopic exchange at 700-840° to be very slightly lowered (by 1-2 kcal/mole) by increasing the specific activity of the $K_2\overset{*}{S}O_4$ preparation from $1.9 \cdot 10^{-2}$ to 1.02 mC/g.

A second system involving heterogeneous isotopic exchange under radioactive irradiation has been studied by Spitsyn and Finikov. It has been shown earlier [8] that isotopic exchange occurs between free oxygen and the sulfates of the alkali metals, at high temperature. In these experiments, sodium sulfate was activated with various amounts of radioactive S^{35} so that its specific activity would be 1.25; 1.5; 1.6; or 1.9 mC/g. The gaseous oxygen contained 1.3-2.2 atom.% of O^{18}. The isotopic exchange of the oxygen was studied by a dynamic method in the temperature interval 680-790° and was checked by the use of the mass spectrometer. The degree of exchange was determined after 8 hours. The experimental conditions were the same as those described in the above cited work. The experimental results showed a sharp increase in the degree of exchange at a $Na_2\overset{*}{S}O_4$ activity of 1.25 mC/g, comparison being with the inactive preparation. The values of the exchange were approximately the same at specific activities of 1.25-1.6 mC/g. Increasing the specific activity of the $Na_2\overset{*}{S}O_4$ to 1.9 mC/g once more decreased the rate of exchange (Fig. 3).

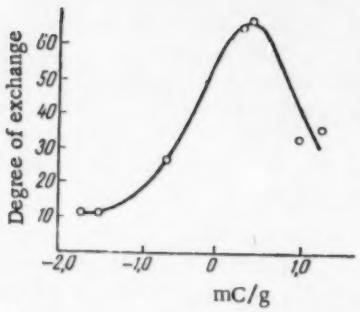


Fig. 2. The relation between the degree of isotopic exchange and the logarithm of the specific activity of $K_2\overset{*}{S}O_4$.

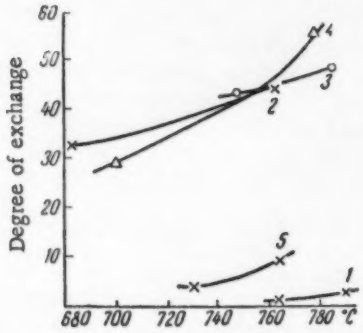


Fig. 3. The effect of the specific activity of sodium sulfate on the degree of isotopic exchange of oxygen in the $Na_2\overset{*}{S}O_4-O_2$ system: 1) inactive; 2) 1.25 mC/g; 3) 1.5 mC/g; 4) 1.6 mC/g; 5) 1.9 mC/g.

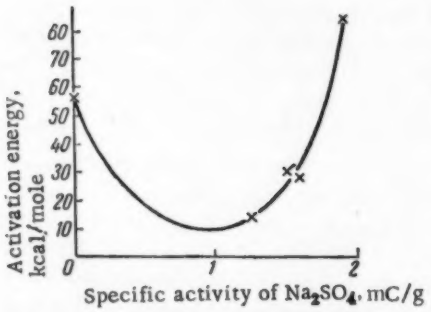


Fig. 4. The relation between the activation energy for the exchange of oxygen in the $Na_2\overset{*}{S}O_4-O_2$ system (680-790°) and the specific activity of the sodium sulfate.

In these experiments, it was difficult to avoid a certain lack of uniformity in regard to the size of the crystals in the preparations of sodium sulfate which were employed. On the other hand, the experimental technique was such as to permit the kinetics of the processes in question to be determined with high accuracy. Thus evaluation was made of the energy of activation of the respective exchange reactions over the investigated interval of temperatures (Fig. 4). The results showed that the energy of activation falls to 12 kcal/mole at a specific activity of $Na_2\overset{*}{S}O_4$ of 1.25 mC/g, i.e., that it diminishes by a factor of 1/4.5 in comparison with the inactive material. A further increase in the specific activity to 1.5-1.6 mC/g results in increasing the activation energy to 28-30 kcal/mole. Finally, at a specific activity of the $Na_2\overset{*}{S}O_4$ of 1.9 mC/g, the activation energy is raised to 85 kcal/mole. The effect of radioactive irradiation on the rate of isotopic exchange was the same here as that which had been observed in the exchange of sulfur in the $K_2SO_4-SO_3$ system, and obviously arose from the same causes. The very existence of the considerable variation in the energy of activation is a fact calling for further experimental investigation.

It was also of interest to observe directly the effect of the solid phase specific activity on processes of adsorption from liquid and gaseous media. For this purpose, Spitsyn and Gromov made use of the much studied $BaSO_4$ – Methylene blue system. Preparations of barium sulfate were obtained through the interaction of solutions of $BaCl_2$ and Na_2SO_4, constancy of conditions being strictly maintained [9]. The last named compound contained the requisite amount of S^{35} tagged sodium sulfate. The precipitate was washed free of Ba^{2+}, Na^+, and Cl^-, ions with distilled water (check was carried out on the Cl^- ions), twice washed with acetone and alcohol, and then dried for 10 hours at 60-70°. The particle dimensions in these precipitates were determined microscopically under a magnification of 900 ×. Data on the specific surfaces, and specific activities, of the precipitates are presented in Table 3.

For studying the sorption, 3 g specimens of the precipitates were shaken with 15 ml portions of Methylene blue solutions of various concentrations (10, 25, 50, 100 and 200 mg/liter, pH 4-5.5) for 4 hours, a 1 hr period being sufficient for the establishment of equilibrium. The equilibrium dye concentrations were determined spectrophotometrically. The sensitivity of the instrument which was employed (SF-4) exceeded the experimentally observed alteration in the dye concentration by 20 fold. Each isotherm was developed from three sets of data. The experimental errors did not

exceed 3-6%. The results of these experiments are shown in Fig. 5.

TABLE 3

Investigated $BaSO_4^*$ Preparations

Specific activity of precipitate, in mC/g (± 10%)	0	0.01	0.1	1
Specific surface of precipitate, in m^2/g (±10-15%)	0.676	0.684	0.590	0.692

It was conceivable that the Methylene blue in solution was partially decolorized by the action of the radioactive irradiation. Special experiments showed that there was no ground for such fear under our working conditions. An effect of this kind became detectable only after 20 hours and with a 100 fold excess activity in the solution. Even with a 0.01 mC/g specific activity in the $BaSO_4$ precipitate there was a decrease in the sorption amounting to approximately 14% of the sorption of the inactive preparation. Increasing the specific activity of the sorbent to 0.1, and to 1 mC/g, led to further dimunition of the amount of the adsorbed Methylene blue by 21%, and by 37%, of the initial value, respectively.

This new information concerning the effect of radioactive irradiation on the physical chemical properties of solid bodies gave grounds to suppose that a similar effect would be noted in catalytic processes as well. Balandin, Spitsyn, Dobrosel'skaia and Mikhailenko studied the rate of the dehydration of cyclohexanol over the temperature interval 335-415° and on a mixed $MgSO_4$, Na_2SO_4 catalyst. This catalyst various amounts of S^{35} had been introduced in the form of radioactive sodium sulfate. In each case, the yield of cyclohexene was compared for two catalysts of the same composition, one inactive and the other containing S^{35}.

These investigations were carried out in a catalytic system of the flow type [10]. The catalytic tube, and the detachable reactor which was joined to it by a ground joint, were prepared from quartz. The cyclohexanol was introduced into this tube from an injector which was equipped for automatically feeding the liquid at a steady rate of 0.22 ml/min. Since cyclohexanol solidifies at room temperature, this injector was warmed by an external jacket which was held at 30°. In each experiment, the reactor was loaded with 0.5 ml of one of the prepared catalysts, the charge weights of these catalysts varying between 0.16 and 0.30 g. The volumetric feed rate was 0.4 min^{-1}. The reaction products were condensed in a receiver through a spiral condenser which had been prepared from molybdenum glass. Each experiment extended over 30 minutes, the catalyzate collected in the first 15 minutes being discarded. Following the Kaufman method of bromine numbers, the degree of conversion of the cyclohexanol was determined by titrating a weighed quantity of the catalyzate which had been obtained in the second 15 minutes after beginning the experiment. After each experiment, the catalyst was regenerated for 45 minutes in a current of dry air flowing at a velocity of 9 liters/hr.

An IMA-1 intensiometer for tagged atoms which had been designed for the determination of soft β-radiation was so inserted into the apparatus as to follow the receiver with the catalyst. The formation of gaseous reaction products containing S^{35} was never observed. Radioactivity was detected in the catalyzate only when the latter had been mechanically contaminated through accidental dispersion of the catalyst.

The experimental results showed that with a specific catalyst activity of 1.26 mC/g, the degree of conversion of the cyclohexanol at 410° was increased by 10%; at 9.2 mC/g there was a 90%, and at 105.2 mC/g,a 180%, increase. The increase in the degree of conversion of the cyclohexanol was proportional to the logarithm of the specific activity of the catalyst (Fig. 6). In Fig. 7 there are presented the results of measurements on the degree of conversion of cyclohexanol with catalysts of various compositions at various temperatures. In each case, the curve for the radioactive catalyst falls above the corresponding curve for the inactive catalyst.

Calculations showed that the apparent energies of activation of this catalytic process were slightly, but definitely, diminished (by 1-2 kcal/mole) by introducing the radioactive isotope, S^{35}, into the catalyst. It can thus be considered as proven that radioactive irradiation of a catalyst at sufficiently high intensity will affect the catalytic activity and the energy of activation of the reaction. It is clear that this rise in the catalytic activity is related to the increase in the number of active centers which is caused by the appearance of defects

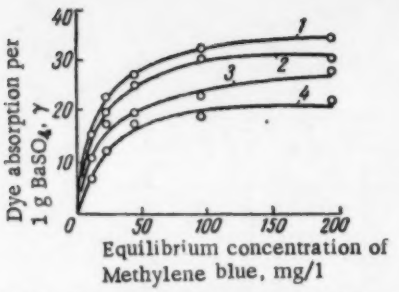


Fig. 5. The sorption of Methylene blue by $BaSO_4$ preparations of various specific activities: 1) inactive; 2) 0.01 mC/g; 3) 0.1 mC/g; 4) 1 mC/g.

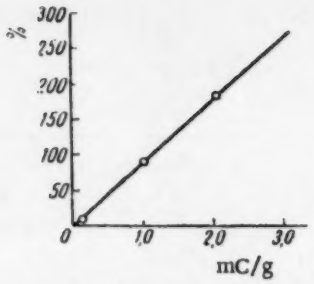


Fig. 6. The relation between the increase in the degree of conversion of cyclohexane and the logarithm of the specific activity of the catalyst.

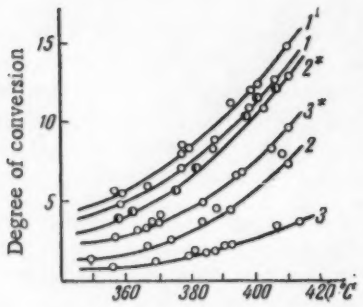


Fig. 7. The effect of the radioactivity of the catalyst on its catalytic activity: 1) $MgSO_4$ + 0.52% Na_2SO_4 (inactive); 1*) $MgSO_4$ + 0.52% Na_2SO_4 (activity – 1.26 mC/g); 2) $MgSO_4$ + 4.06% Na_2SO_4 (inactive); 2*) $MgSO_4$ + 4.06% Na_2SO_4 (activity – 9.2 mC/g); 3) $MgSO_4$ + + 21.87% Na_2SO_4 (inactive); 3*) $MgSO_4$ + + 21.87% Na_2SO_4 (activity – 105.2 mC/g).

in the crystal lattice and on the catalyst surface; it is also related to the action of the β-particles on those active centers which adsorb the molecules of the reacting substance.

SUMMARY

1. The rate of the high-temperature isotopic exchange of sulfur in the $K_2\overset{*}{S}O_4-SO_3$ system, and of oxygen in the $Na_2\overset{*}{S}O_4-O_2$ system, depends significantly on the level of radioactive irradiation (in terms of S^{35}) of the investigated sulfate specimens.

2. Radioactivity has been shown to affect the amount of Methylene blue adsorbed from aqueous solutions by precipitated $Ba\overset{*}{S}O_4$.

3. As an instance of the positive effect of radioactivity on a catalyst, description has been given of the kinetics of the dehydration of cyclohexanol.

The Institute of Physical Chemistry
of the Academy of Sciences of the USSR

Received
July 4, 1958

LITERATURE CITED

[1] E. H. Taylor, and J. A. Wethington, Jr., J. Amer. Chem. Soc. 76, 971 (1954).

[2] E. H. Taylor and H. W. Kohn, J. Amer. Chem. Soc. 79, 252 (1957).

[3] R. W. Clarke and E. J. Gibson, Nature 180, 140 (1957).

[4] P. B. Weisz and E. W. Swegler, J. Chem. Phys. 2[illegible], 1567 (1955).

[5] H. E. Farnsworth and R. F. Woodcock, Advances in Catalysis 9 (1957).

[6] P. Guenther, Ergebn. techn. Roentgenkunde 4, 100 (1934).

[7] Vikt. I. Spitsyn and I. E. Mikhailenko, J. Inorg. Chem. 3, 1254 (1958).

[8] Vikt. I. Spitsyn and V. G. Finikov, Proc. Acad. Sci. USSR 108, 491 (1956).*

[9] A. J. Rutgers and W. van den Henvel, Experientia, 11, Fasc. 12, 481 (1955).

[10] A. P. Rudenko and G. A. Slovokhotova, Factory Labs., No. 1, 121 (1955).

*Original Russian pagination. See C. B. Translation.

THE DEHYDROGENATION OF CERTAIN HYDROAROMATIC HYDROCARBONS ON A CHROMATE CATALYST

A. A. Balandin and G. V. Isaguliants

In the present work, investigation has been made of the dehydrogenation of certain hydroaromatic hydrocarbons on a chromate catalyst, the aim being to obtain comparative data which would be of interest in developing the mechanism of catalytic dehydrogenation. Special efforts were directed to assuring completely uniform reaction conditions for the various hydrocarbons so that the resulting data would be comparable with one another, both qualitatively and quantitatively.

EXPERIMENTAL

This work was carried out by a flow method. The general layout of the apparatus was similar to that which was employed in [1]. The reactor was a tube of hard glass, 18 mm in diameter and 120 cm in length, which was inserted in a thermoregulated tubular furnace. Two constant level graduated gasometers, 250 and 1000 ml in volume, served for collection of the gases [1]. The temperature was measured with an accuracy of 0.2° by a thermocouple which was connected with a thermograph, the thermocouple well being introduced directly into the catalyst bed. The temperature variation in the course of an experiment, both along the catalyst bed and in time, did not usually exceed ±1°.

In this work, much importance is attached to maintaining a constant, and easily reproducible, rate of feed of the working material into the reactor. For this reason there was employed an automatic burette with a piston, from which the rate of liquid delivery could be regulated by a Warren electric motor. The design of this burette was borrowed from [2].

The catalyst was placed in the middle region of the catalytic tube which contained the thermocouple well in its center, the position of the catalyst being fixed by a glass fiber mesh and special supports [1]. This catalyst was continually maintained in an atmosphere of hydrogen, hydrogen being also introduced between experiments for the rapid removal of the reaction products from the zone of the catalyst. The hydrogen which was used for this purpose was introduced into the reactor from an electrolyzer, after having been first passed through a tube containing palladiumized asbestos at 200°, for the removal of traces of oxygen, and then through a sulfuric acid scrubber and a tube filled with granulated alkali.

Before beginning each experiment, the system was tested to be sure that it was gas tight. The experimental operations were carried out in the following sequence: the position of the lower part of the piston in the burette was noted, the level in the gasometer was recorded, and a mark made on the time coordinate of the thermograph, following which the burette was put into action and timing begun. Readings on the actuating burette were made every 10 minutes; the gasometer was read every 1, 2 or 5 minutes, depending on the reaction rate. The volume of the evolved gas was reduced to normal conditions, account being taken of the water level difference in the gasometer at each reading. Each experiment extended over 50-90 minutes. Gasometer readings were made only after the reaction had become stationary, which was usually 5-10 minutes after commencing the experiment.

The various hydrocarbons were introduced into the reaction tube from the automatic burette at an equimolar rate of ~0.001 moles/min. In Tables 3-7 and 9-10, the rate of liquid feed is expressed in millimeters of hydrogen resulting from 100% conversion (A_1). Gas analysis was carried out on the gaseous reaction products:

the hydrogen content of these gases was usually 97-98%, being in no case less than 95%; they were completely free of unsaturated gases and carbon dioxide but contained a certain amount of saturated hydrocarbons which, judged from the considerable volume increase accompanying combustion, represented vapors of the liquid hydrocarbons. The liquid portion of the reaction products was examined for unsaturated compounds (see the corresponding tables), these being determined bromometrically [3]. In addition, the aromatic hydrocarbon, the principal product of dehydrogenation, was separated out, either in the pure form or as derivatives.

It has been shown by Brusov and one of us [4] that the variable activity of pure chromic oxide which has been prepared pyrogenically, or by precipitation, makes it unsuitable for kinetic experiments, whereas chromic oxide which has been precipitated on asbestos is a good dehydrogenation catalyst and gives nicely reproducible results. It was this latter catalyst which was employed here, it being considered that asbestos is the most inert of carriers in regard to dehydrogenation and one which does not interfere, in even the slightest degree, with the action of the chromic oxide.

The technique of preparing the catalyst was taken from [4] and involved reduction of ammonium dichromate by methyl alcohol in the presence of sulfuric acid, followed by precipitation of chromic hydroxide with ammonia, this precipitate being washed with distilled water and dried in air and in a current of hydrogen. The dichromate which was used here was the Russian product of analytical grade which preliminary analysis had shown to be free of iron. The asbestos was from asbestos braid, and was washed in nitric acid, then carefully rewashed in water and dried in air. The catalyst contained 50% of chromic oxide by weight.

The catalyst taken in each experiment made up 4 g (10 ml), the length of the catalyst bed being 5 cm. This catalyst had a constant activity which was checked against the dehydrogenation of cyclohexane.

EXPERIMENTAL RESULTS

Cyclohexane was the first material investigated in these experiments. Although the dehydrogenation of this compound on oxide catalysts, chromic oxide included, has been subjected to repeated qualitative and quantitative study, it was considered necessary to repeat and extend these investigations. The reasons for doing this

TABLE 1

Constants of the Hydroaromatic Hydrocarbons

Hydrocarbon designation	B.p., in °C	n_D^{20}	d_4^{20}
Cyclohexane	79,5—79,8	1,4264	
Methylcyclohexane	99,0—99,4	1,4250	0,7707
1,3-Dimethylcyclohexane	119,5—120,5	1,4242	
Tetralin	207,6—208,2	1,5419	0,9713
Methyltetralin	229,6—230,1	1,5345	0,9543

were twofold; first, there was the necessity of finding a point of contact with work which was already available, and, second, there was the need for a standard which might serve in fixing the activity of the catalyst. Experiments with the other hydroaromatic hydrocarbons; methylcyclohexane, 1,3-dimethylcyclohexane, tetrahydronaphthalene, and 2-methyl-5, 6, 7, 8-tetrahydronaphthalene, were carried out under exactly the same conditions: the activity of the catalyst was checked against cyclohexane prior to beginning experiments with each hydrocarbon, and proved to be constant in all cases except those which will be specially noted later.

The experimental hydroaromatic hydrocarbons were prepared by hydrogenation of the corresponding aromatic hydrocarbons in an autoclave above a Raney nickel catalyst. The constants of these hydrocarbons are given in Tables 1 and 2.

In each experiment, invariance of catalytic activity would be indicated by constancy of the rate of evolution of gas, at constant temperature and rate of feed; that this condition was actually fulfilled is shown by Figs. 1-5 in which time is plotted as the abscissa, and volume of evolved gas as the ordinate. In addition, the above

TABLE 2

Constants of the Aromatic Hydrocarbons Selected for Hydrogenation

Hydrocarbon designation	B.p., in °C	M.p., in °C	n_D^{20}	d_4^{20}
Benzene			1,5010	
Toluene	109,5—110,4		1,4967	0,8664
m-Xylene	138,7—139,5		1,4976	0,8639
Naphthalene		81,0		
Methylnaphthalene		35,0		

mentioned control experiments showed that each portion of the catalyst could repeatedly dehydrate the various hydrocarbons without decrease in activity.

The results of these experiments are presented in Tables 3-7. The m column gives the rate of reaction, expressed in millimeters of H_2 (STP) per 1 minute per 1 ml of catalyst. The remaining column headings require no explanation. The term A_1 in these headings designates the rate of feed of the working substance into the catalyst tube. The percentage conversion is to be found from the value of m/A_1.

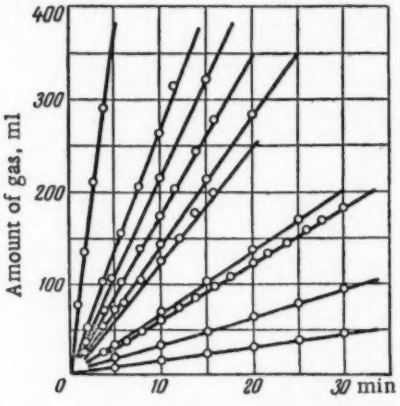


Fig. 1. Constancy of catalytic activity in experiments with cyclohexane.

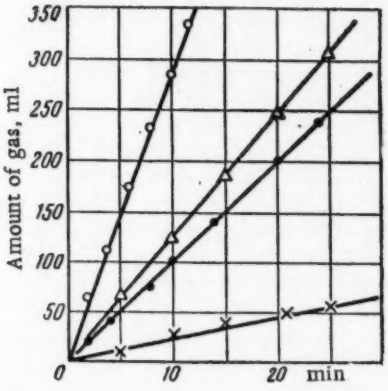


Fig. 2. Constancy of catalytic activity in experiments with methylcyclohexane.

TABLE 3

The Dehydrogenation of Cyclohexane (Amount of catalyst, 10 ml (4 g); length of bed, 5 cm; A_1 = 63.5 ml H_2/min)

Expt. no.	Temp., °C	$m \cdot 10^2$	Degree of conversion, %	$n^{20}D$ of catalyzate
49	400	30	4,7	—
46	413	36	5,7	1,4295
48	427	66	10,4	1,4297
47	450	105	16,6	1,4332
50	472	167,5	26,2	—

TABLE 4

The Dehydrogenation of Methylcyclohexane (Amount of catalyst, 4 g; A_1 = 67.0 ml H_2/min)

Expt. no.	Temp., °C	$m \cdot 10^2$	Degree of conversion, %	Cont. of unsat. comp'ds in catalyzate, %
211	408	30	4,47	—
208	419	43,5	6,4	3,7
209	446	80	11,9	3,1
212	465	100	16,1	—
210	474	140	21	3,8

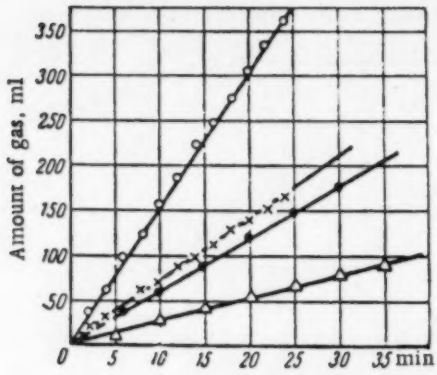


Fig. 3. Constancy of catalytic activity in experiments with dimethylcyclohexane.

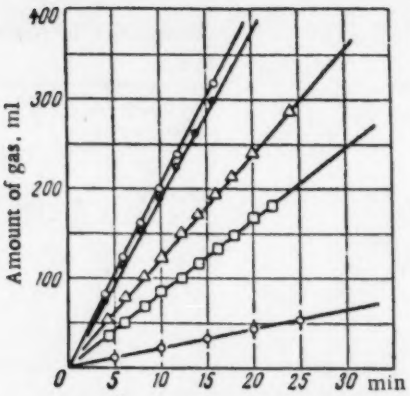


Fig. 4. Constancy of catalytic activity in experiments with tetralin.

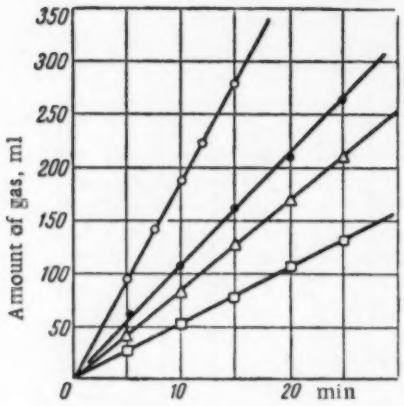


Fig. 5. Constancy of catalytic activity in experiments with methyltetralin.

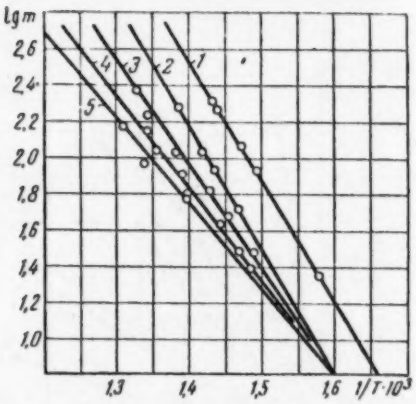


Fig. 6. The relation between the temperature and the amount of product hydrogen: 1) tetralin, 2) methyltetralin, 3) cyclohexane, 4) methylcyclohexane, 5) dimethylcyclohexane.

Figure 6 presents the relation between the reaction rate and the temperature, in graphic form. In each case, the points fall on a straight line, so that the variation of the rate of dehydrogenation with temperature follows the Arrhenius Law. The three lower lines, 3, 4, and 5, are ones referring to the three cyclohexanes. The line for the dimethylcyclohexane is lower, and more inclined than are the others.

The lines corresponding to the two tetralins lie considerably above those for the cyclohexanes. Under similar conditions, and in a like period of time, tetralin evolves a larger volume of hydrogen than does cyclohexane. This is made the more striking if, instead of log m, the logarithm of the percent conversion is plotted as the ordinate, expression being thereby given to the fact that cyclohexane evolves 3 molecules of hydrogen in dehydrogenation, and tetralin only 2.

In Fig. 7, Arrhenius lines have been plotted for tetralin (1), methyltetralin (2) and cyclohexane (3), the logarithm of the degree of conversion in percentages being given on the axis of ordinates. By comparing the results of experiments which were carried out at the same temperature, it can be concluded that the rate of dehydrogenation of tetralin is approximately six times greater than that of cyclohexane (Table 6, Experiments Nos. 74 and 89). Taking into account the fact that the position of the Arrhenius line is characterized by the values of k_0 and Q, it can be said that there is an increase in the energy of activation, and a decrease in the constant k_0, as substituents are added to form the three cyclohexanes.

TABLE 5

The Dehydrogenation of 1,3-Dimethylcyclohexane
(Amount of catalyst, 4 g; A_1 = 67.0 ml H_2/min)

Expt. no.	Temp., °C	$m \cdot 10^3$	Degree of conversion, %	Cont. of unsat. comp'ds in catalyzate, %
51	400	24,4	4,0	1,65
52	441	64	10,5	1,6
55	442	59	9,7	—
54	474	91	14,9	2,45
53	491	150	24,6	1,82

TABLE 6

The Dehydrogenation of Tetrahydronaphthalene
(Amount of catalyst, 4 g; A_1 = 41.5 ml H_2/min)

Expt. no.	Temp., °C	$m \cdot 10^3$	Degree of conversion, %	Cont. of unsat. comp'ds in catalyzate, %
73	360	22	5,3	
72	396	85	20,5	1,5
75	405	116	27,9	
78	405	113	27,2	
81	421	185	44,6	
71	424	203	48,8	2,0
74	425	200	48,3	
89	423	50	7,9	

TABLE 7

The Dehydrogenation of 2-Methyl-5, 6, 7, 8-tetralin
(Amount of catalyst, 4 g; A_1 = 41.5 ml H_2/min)

Expt. no	Temp., °C	$m \cdot 10^3$	Degree of conversion, %	Cont. of unsat. comp'ds in catalyzate, %
173	407	52	9,6	
175	424	84	20,3	4,5
174	429	108	26,0	4,7
172	448	188	45,3	2,4

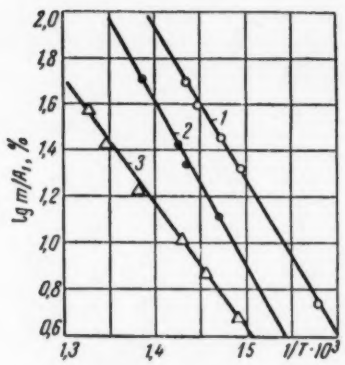


Fig. 7. The relation between the temperature and the degree of conversion of tetralin (1), methyltetralin (2) and cyclohexane (3).

Table 8 gives values of the apparent energy of activation, Q, the logarithm of the constant k_0, and the dispersion constant $1/a = Q/\log k_0$, invariance of the latter being characteristic of a logarithmic relation between Q and k_0 [5]. This value of 1/a is characteristic of the oxide catalysts [5].

Interesting results were obtained on the dehydrogenation of cyclohexane and tetralin on a catalyst of diminished activity. An approximate 20% reduction in the activity with respect to cyclohexane occurred after extended work with the catalyst and repeated regeneration. In Table 9 there are given results from the dehydrogenation of cyclohexane on such an exhausted catalyst, all of the experimental conditions being the same as those of the experiments of Table 3. The data of these tables is represented graphically in Fig. 8, the line covering the data of Table 9 (3) falling lower than that for the data of Table 3 (2). It is a curious fact that rate differences were not observed for the dehydrogenation of tetralin on this same catalyst, the data from the experiments of Table 10 falling exactly on the line for the active catalyst of Table 6 (1); in Fig. 8 the former points are designated as +.

From this it can be concluded that tetralin dehydrogenates on a greater number of active centers than does cyclohexane. For all of these surfaces which are active in the dehydrogenation of cyclohexane, the mean value of Q, as given in Table 8, is less than the corresponding value for those surfaces which are active for the dehydrogenation of tetralin. From this it follows that the regions required for the dehydrogenation of cyclohexane are of higher activity than is the case for the dehydrogenation of the tetralin. On the other hand, a comparison of the values of k_0, a quantity involving the magnitude of the active surface as a multiplying factor, for the two types

TABLE 8

Values of the Apparent Energy of Activation, and the Multiplying Factor, for the Dehydrogenation of Various Hydrocarbons

Hydrocarbon designation	Q, in kcal/mole	$\lg k_0$	1/a
Cyclohexane	25 900	9,89	2,62
Methylcyclohexane	23 700	9,08	2,62
Dimethylcyclohexane	22 200	8,5	2,62
Tetralin	29 700	11,4	2,62
Methyltetralin	30 400	11,5	2,64

TABLE 9

The Dehydrogenation of Cyclohexane (Exhausted catalyst)
(A_1 = 63.5 ml H_2/ min; amount of catalyst, 4 g; Q = 25,700 cal/mole)

Expt. No.	Temp. °C	$m \cdot 10^3$	Degree of conversion, %
107	433	44	6,9
105	436	59,5	9,4
104	460	108	17,0
108	471	127	20,0
106	494	237	37,5
50*	472	167,5	26,2

*The activity of the catalyst was lower than in the experiments described earlier. For comparison, Experiment No. 50, from Table 1, has been inserted at the end of Table 9.

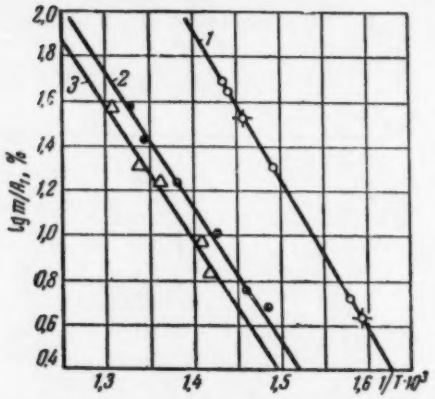


Fig. 8. The relation between the degrees of conversion of tetralin, and cyclohexane, on fresh, and on "exhausted," catalysts: 1) tetralin; 2) cyclohexane on fresh catalyst; 3) cyclohexane on exhausted catalyst.

TABLE 10

The Dehydrogenation of Tetralin (Exhausted catalyst)
(A_1 = 415 ml H_2/min; amount of catalyst, 4 g)

Expt. No.	Temp. °C	$m \cdot 10^3$	Degree of conversion, %
110	356	18	4,4
109	416	142	34,2

of hydrocarbons makes it clear that the active surface is many times greater for the tetralin than for the cyclohexane. This detail explains the enhanced reactivity of tetralin as compared with cyclohexane.

The process leading to a diminution of the activity of the catalyst which has been referred to earlier, first takes the more active regions out of play. But although this lowers the activity of the catalyst for cyclohexane by 20% (according to the experimental data of Tables 1 and 7), it is so insignificant in the case of tetralin as to fall outside the sensitivity of the measurements.

SUMMARY

1. Investigation has been made of the dehydrogenation of cyclohexane, decalin, methylcyclohexane, 1,3-dimethylcyclohexane, tetralin and 2-methyl-5, 6, 7, 8-tetrahydronaphthalene on a chromate catalyst. This is the first time that such a study has been carried out on the last four of these compounds. Energies of activation were determined for the dehydrogenation of cyclohexane, 1,3-dimethylcyclohexane, methylcyclohexane, tetralin and methyltetralin on chromic oxide.

2. The structurally closely related hydrocarbons cyclohexane, methylcyclohexane, dimethylcyclohexane, and decalin, are characterized by Arrhenius constants which are approximately the same, but not identical, in

value. The appearance of the methyl groups in the cyclohexane ring somewhat diminishes the values of these constants, this, in turn, leading to marked differences in the rates of dehydrogenation at high temperatures.

3. Tetralin and methyltetralin are capable of being dehydrogenated on a larger number of active sectors than is the case with cyclohexane and its homologs, the dehydrogenation being characterized by higher values of the Arrhenius constants.

4. For the dehydrogenation of each of these hydrocarbons, the multiplying factor is logarithmically related to the energy of activation. The dispersion constant is the same in all cases.

The N. D. Zelinskii Institute of Organic Chemistry
of the Academy of Sciences of the USSR

Received May 14, 1957

LITERATURE CITED

[1] A. A. Balandin and A. Bork, Z. Phys. Chem. 33, 54 (1936).

[2] A. Oblad, R. Marschner and L. Heard, J. Amer. Chem. Soc. 62, 2066 (1940).

[3] Rosenmund and Kuhntenn, Z. für Untersuch. d. Nahrungs und Genussmittel 46, 154 (1923).

[4] A. A. Balandin and I. I. Brusov, J. Gen. Chem. 7, 37 (1937).

[5] A. A. Balandin, J. Phys. Chem. 4, 257 (1933).

OVERVOLTAGE IN THE ELECTRODEPOSITION OF ANTIMONY

A. P. Popkov, V. M. Gevorkian and A. T. Vagramian

The study of the rate of discharge of antimony, and the determination of the overvoltage of its deposition, present special difficulties because of the uncertainty in the values of the equilibrium potential. Freshly deposited antimony undergoes rapid oxidation when brought into contact with a solution, and its equilibrium potential is thereby displaced in the positive direction, the magnitude of this displacement depending on the composition of the solution and the hydrogen ion concentration, and on other factors as well [1]. It is clear that this uncertainty in the stationary potential makes for difficulty in obtaining exact values of the overvoltage by the customary methods. The present work has studied the polarization during electrodeposition of antimony by a rapid method in which the displacement in the equilibrium potential could be so taken into account as to give a more exact determination of the voltage.

EXPERIMENTAL

The experimental determination of the overvoltage of deposition of antimony was carried out in a hermetically sealed cell of 50 ml volume. A platinum wire, fused into glass, served as the cathode. The surface area of this cathode was $2 \cdot 10^{-3}$ cm^2. The anode was a platinum wire, S = 0.5 cm^2, covered with a thick layer of electrolytic antimony. In measuring the potential, the end of the capillary of the electrolytic bridge was brought up to the cathode and held at a fixed distance from it. The overvoltage of the deposition of antimony was studied in antimony tartrate and chloride solutions. Each experiment was carried out in a thermostat at 20°. Prior to each measurement, the cathode surface was covered with a dense layer of antimony, 10-15μ in thickness, using a $K(SbO)C_2H_4O_6$, 50 g/liter, electrolyte of pH 1.7-2 with i_c = 5-8 ma/cm^2.

In developing the polarization curves by the rapid method [2], a resistance of $\sim$500 kΩ was placed in the external circuit in series with the electrolytic cell, the aim being to avoid distortion of the linear variation of the current strength through polarization of the electrode. The polarization curves were recorded on film (9 × 25 cm) by using a short-period mirror galvanometer with a natural frequency of oscillation of 100 vib/sec.

DISCUSSION

Preliminary experiments on the electrodeposition of antimony had shown that dense, finely-crystalline, precipitates could be obtained in acidified antimony tartrate solutions, at yields of practically 100%. Since these electrolytic deposits of antimony were smooth and uniform, it could be supposed that the geometrical electrode surface was essentially unaltered by the electrolysis, and differed by little from the true surface. It should be noted that the total surface of the electrode would be constant over the brief interval of time corresponding to the development of a polarization curve.

In Fig. 1a there is shown a photograph of an oscillogram of polarization curves which had been developed by the rapid method. Figure 1b gives these same curves and the requisite notation. Here the polarization (φ_c) is plotted on the axis of ordinates, and the current density (i_c), on the axis of abscissas.

Curves 1, 2, 3, and 4 were developed at the respective velocities of 0.48; 4; 15.6 and 31.2 cm/sec. The curve cycles, from zero to maximum current density, and from maximum to zero; are, respectively, 28; 3; 0.86 and 0.43 sec. Each of these curves was repeatedly developed. It is to be seen from Fig. 1b that polarization curve

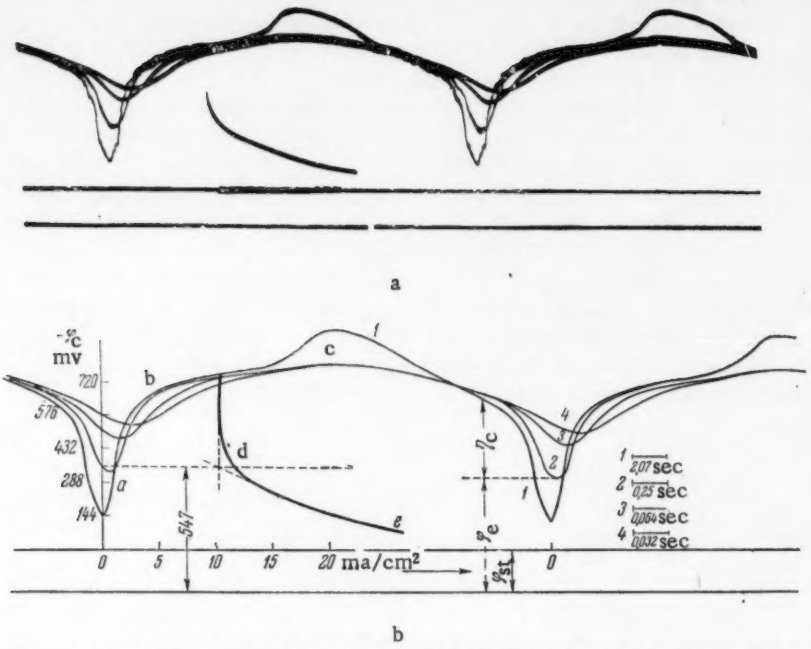


Fig. 1. a) Oscillogram developed during the electrodeposition of antimony from a $K(SbO)C_2H_4O_6$ 50 g/liter solution, pH 3.55, b) polarization curves developed during the electrodeposition of antimony, i_{max} = 20 ma/cm²; φ_c) cathodic polarization; η_c) overvoltage for the deposition of antimony; φ_e) equilibrium potential of a freshly deposited antimony surface; φ_{st}) stationary potential (measured against a saturated calomel electrode) of a Sb/Sb_2O_3 electrode in the given solution.

1, which had been developed at low velocity, was essentially different from the other curves. Thus an increase in the current density from 0 to 2.5-3 ma/cm² (section ab), was accompanied by a sharp rise in the cathodic polarization, following which the polarization altered only insignificantly up to a density of 13-15 ma/cm², where there was a further rise as the result of initiation of concentration polarization. Curves 2, 3, and 4, were developed at higher velocities and are practically identical at maximum current density, deviation being substantial only at the lower current densities where it becomes especially marked as the density approaches zero. The slower the development of the curve, the greater is the positive displacement of the equilibrium potential of the electrode. It is likely that this effect is related to the oxidation of the antimony surface which takes place at lower current densities and $i_c = 0$, the potential being shifted in the positive direction. It is clear that the value of the overvoltage (η_c) determined relative to the stationary potential (φ_{st}) representing the difference between the potential of the auxiliary electrode and the steady value of the potential of the antimony electrode in the given solution, will differ considerably from the overvoltage determined relative to the equilibrium potential (φ_e) corresponding to a freshly precipitated, active antimony surface. It is thus clear that the accuracy of the determination of the overvoltage is fixed by that of the determination of the true value of the equilibrium potential. Thus, when the equilibrium potential of the electrode is taken as −331 mv (Curve 1), the overvoltage at i_c = 15 ma/cm² will be −638 mv, whereas working from Curve 3 and considering the equilibrium electrode potential to be −622 mv, the overvoltage would be −302 mv at this same current density. The overvoltages resulting from these data would thus differ by a factor of more than 2.

It is useful to divide the polarization curves into two segments, ab and bc. There is a marked difference in the slopes over these curve segments. At low current densities (segment ab), the slope of the polarization curve is considerably greater than it is in the region of high current densities (segment bc). As Fig. 1b shows, the slope of the ab segment diminishes with increasing rate of development of the curves and approaches that of the

segment bc (Curves 2, 3, and 4). The unusually high value of the slope of the curve segment ab probably results from the fact that the rate of surface oxidation becomes comparable with the rate of deposition when the current density is low and the curve is slowly developed, the results being that the electrode potential is displaced in the positive direction and there is an increase in the slope of the polarization curve. The oxidation of the electrode surface diminishes as the rate of developing the curve is increased, and the slope of the segment ab approaches that of the segment bc. Thus on a polarization curve which has been developed at high velocity, it is to be expected that the electrode potential at i = 0 would be the equilibrium potential corresponding to the active state of the surface. However, trust cannot be placed in those values of the equilibrium potential which are obtained at very high velocities, when the whole of the polarization curve from 0 to i_{max} is developed in 0.2-0.4 sec. (Curves 3 and 4) since it is possible for antimony to separate out in a metastable form (α-antimony) which subsequently passes into the ordinary modification [3]. The metastable form of the metal has a more negative potential than does the stable modification, so that the equilibrium potential obtained from a rapid development of the curve is somewhat too high in value. If it is further supposed that a finite period is required for discharge of the electric double layer after cutting off the current, it would then follow that the electrode potential obtained from rapidly developed polarization curves, at i = 0, would be displaced in the negative direction. It will be shown below that the approximate value of the equilibrium potential must be ~ −550 mv (dotted line in Fig. 1b).

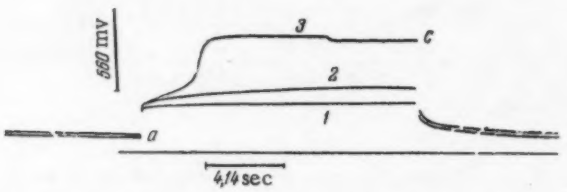


Fig. 2. Oscillogram developed during the electrodeposition of antimony in a $K(SbO)C_2H_4O_6$ 50 g/liter solution pH 2, at various current densities; a) point at which the polarization current was turned on; c, point at which the current was cut off.

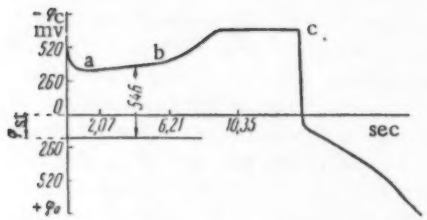


Fig. 3. The change in the polarization of the cathode following a preliminary 20 sec anodic polarization of the antimony electrode in a $K(SbO)C_2H_4O_6$ electrolyte of pH 3.55, at i_c = = 2.2 ma/cm^2.

This value of the equilibrium potential is obtained from the curve showing the fall in potential after opening the circuit. If it is supposed that the first gradual fall-off in this curve (segment de) is associated with the beginning of oxidation of the electrode surface, the equilibrium potential corresponding to a freshly deposited antimony surface can then be evaluated by extending the tangents to intersection. If the gradual fall-off of the potential after opening the circuit is due to the oxidation of the antimony surface, it should always be observed at the same values, regardless of the polarization of the electrode. As Fig. 2 shows, the beginning of oxidation of the antimony is actually independent of the absolute value of the polarization of the electrode. Curves 1, 2, and 3 were developed at various current densities, and correspond to different cathodic polarizations, but nevertheless the fall-off of the potential, after opening the circuit, (point c) begins for all of the curves at essentially the same point, which is that corresponding to the initiation of oxidation of the freshly deposited antimony. Indirect indication that this is the potential value corresponding to the passage of the antimony surface from an active into a passive state is to be found in the following experimental data. If the surface of electrolytically deposited antimony is given in a preliminary oxidation by being subjected to anodic polarization, and the passive electrode then polarized cathodically at low current densities, a retardation, ab, is observed on the polarization curve at φ = −546 mv (Fig. 3). No such retardation is to be observed without this preliminary oxidation of the surface for the polarization then immediately takes on the

value corresponding to the existing current density. The presence of this retardation on the cathodic branch of the polarization curve is clearly related to the reduction of the oxide which was formed during anodic polarization, this reduction preceding the deposition of the metal.

Since the value of the reduction potential of the oxide, −546 mv, practically coincides with the beginning point of the gradual fall-off in the potential, it can be concluded that reduction proceeds at the reversible potential, the displacement in the positive direction after cutting off the current being due to the oxidation of the surface. It follows that the equilibrium potential of a freshly deposited antimony surface must be approximately φ_e = 540-550 mv (Fib. 1b, dotted line). If the displacement of the equilibrium potential in the positive direction is due to surface oxidation, what has been said would indicate that the rate of this oxidation would then be lower in more acidic solutions, with the result that the displacement of the equilibrium potential would also be smaller. In Fig. 4 there are shown polarization curves which were developed in more acidic solutions. From this figure, it is seen that the displacement of the equilibrium potential in the negative direction is much less here. The diminished displacement of the equilibrium potential is accompanied by a decrease in the absolute value of the overvoltage. The observed parallelism between the displacement of the equilibrium potential and the decrease in the overvoltage is to be explained by a diminution in the retarding action of the antimony oxide which is formed on the cathode surface. The polarization curves obtained in the electrodeposition of antimony from chloride solutions are completely different (Fig. 5). Here, the displacement of the equilibrium potential at i = 0 does not exceed −25 mv. In this case, the absolute value of the overvoltage for the deposition of antimony at i = 15 ma/cm² is −80 mv, whereas, at the same current density, the overvoltage for the deposition of antimony from tartrate solutions is −400 mv. The slope of the polarization curve for the deposition of antimony in chloride solutions is 60-65 mv; that for the deposition of antimony in tartrate solutions, −360 mv. On the basis of these

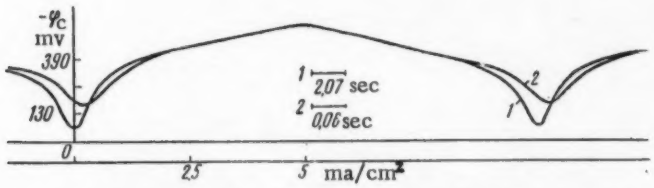


Fig. 4. Polarization curves for the electrodeposition of antimony from a $K(SbO)C_2H_4O_6$ 50 g/liter solution, pH 2, at i_{max} = 5 ma/cm².

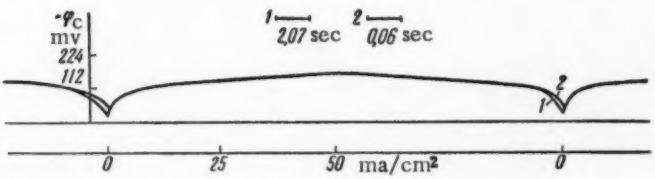


Fig. 5. Polarization curves for the electrodeposition of antimony from a $SbCl_3$ 100 g/liter solution, pH 0.3, at i_{max} = 50 ma/cm².

data it can be concluded that the rate of reduction of antimony in chloride solutions is several orders higher than that for the reduction in tartrate solutions.

SUMMARY

1. By using the rapid method for the development of polarization curves, those difficulties in the determination of the equilibrium potential of antimony which arise from oxidation of the electrode surface can be avoided and a more accurate evaluation of the overvoltage for the deposition of the metal becomes possible.

2. Determinations of the overvoltage for the electrolytic deposition of antimony have shown that this quantity is considerably greater for deposition from tartrate solutions than it is for deposition from chloride solutions.

The Institute of Physical Chemistry of the
Academy of Sciences of the USSR

Received April 15, 1957

LITERATURE CITED

[1] Monograph, The Rare Metals, Antimony, (in Russian), Moscow, Foreign Lit. Press, 1954; E. N. Vinogradov, Methods for Determining the Concentration of Hydrogen Ions (in Russian), Moscow, Moscow State University Press, 1956.

[2] A. T. Vagramian, The Electrodeposition of Metals (in Russian), Moscow, Acad. Sci. USSR, 1950.

[3] V. Steinwehr and M. Schulze, Z. Phys. 63, 815 (1930).

*Russian translation.

SYNTHESIS OF ORGANOMERCURY COMPOUNDS FROM HYDRAZONES

COMMUNICATION 1. REACTION OF HYDRAZONES OF ALIPHATIC ALDEHYDES AND KETONES WITH MERCURIC ACETATE

A. N. Nesmeianov, O. A. Reutov, A. S. Loseva and M. Ia. Khorlina

Hydrazones – a readily available class of organic compounds – have not as yet been used for the synthesis of organometallic compounds. In this paper it is shown that hydrazones react readily with mercuric acetate at moderate temperatures (in the cold or at 70-90°) in water, methanol or absolute benzene with the formation of nitrogen, mercurous salts and organomercury compounds. The reaction is of the "conjugated addition" type. Besides the oxidation of the hydrogen atoms of the hydrazone group, addition of an acetomercuric group to the valences freed by the evolution of nitrogen takes place, also the appropriate electronegative group depending on the solvent: in water a hydroxyl group is added; in methanol, a methoxy group; in absolute benzene, an acetoxy group. In water, however, not α-hydroxyalkyl mercury derivatives but mercurated derivatives of ethers are formed.

The above reactions can be represented by the following equations:

1) In water:

$$2RR'C=N-NH_2+6Hg(OCOCH_3)_2+H_2O\rightarrow 6CH_3COOH+2N_2+$$
$$+2Hg_2(OCOCH_3)_2+\left(RR'C(HgOCOCH_3)\right)_2O. \qquad (1)$$

2) In methanol:

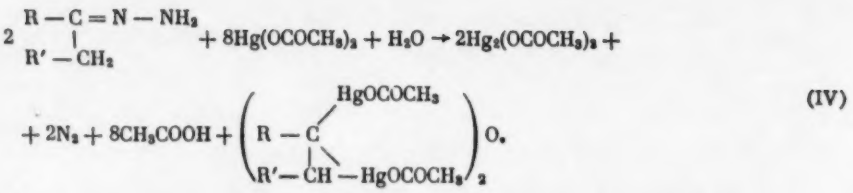
$$RR'C=N-NH_2+3Hg(OCOCH_3)_2+CH_3OH\rightarrow 3CH_3COOH+N_2+$$
$$+Hg_2(OCOCH_3)_2+RR'C(HgOCOCH_3)(OCH_3) \qquad (II)$$

3) In absolute benzene:

$$RR'C=N-NH_2+3Hg(OCOCH_3)_2\rightarrow 2CH_3COOH+N_2+$$
$$+Hg_2(OCOCH_3)_2+RR'C(HgOCOCH_3)(OCOCH_3) \qquad (III)$$

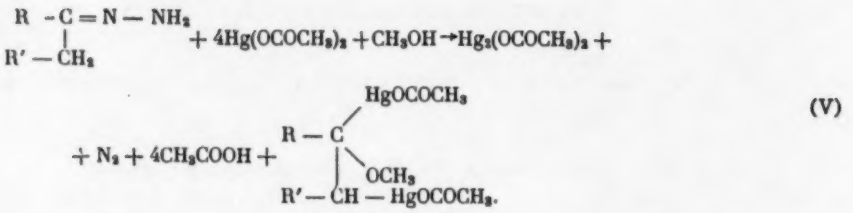
In the majority of the reactions between hydrazones and mercuric acetate that we have examined, dimercurated compounds are formed independently of whether an equivalent quantity or a deficiency of mercuric acetate is used:

4) In water:



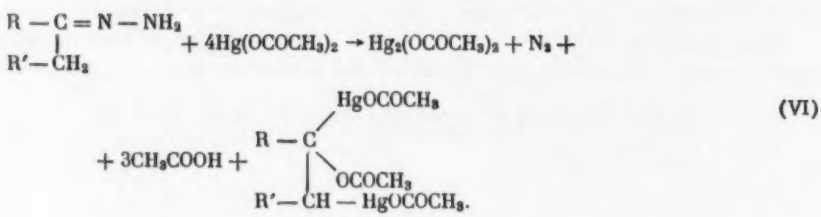
(IV)

5) In methanol:



(V)

6) In absolute benzene:



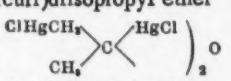
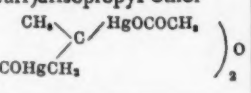
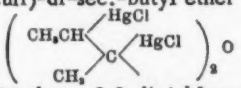
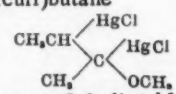
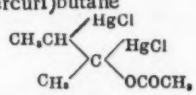
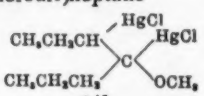
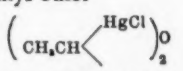
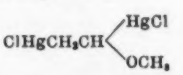
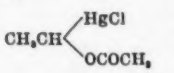
(VI)

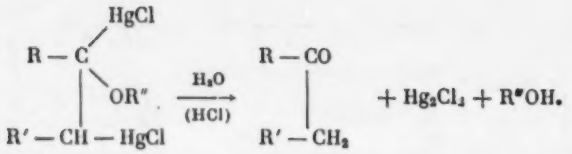
In this investigation the reactions of hydrazones of aliphatic ketones and aldehydes (acetaldehyde, acetone, methylethyl ketone and butyrone) with mercuric acetate were studied in water, methanol and absolute benzene. Acetaldehyde hydrazone reacts with mercuric acetate in water according to Equation (1), in methanol according to Equation (5) and in benzene according to Equation (3); acetone hydrazone in water, ethanol and absolute benzene reacts according to Equation (4) in all three cases. This can obviously be explained by acetone hydrazone reacting in the form of the hydrate. Methylethyl ketone hydrazone reacts with mercuric acetate according to the following equations: in water according to (IV), in methanol according to (V) and in benzene according to (VI). Butyrone hydrazone reacts with mercuric acetate in methanol according to Equation (5). The organomercury compounds formed from those reactions carried out in absolute benzene and in water could not be isolated in the pure state because of their extreme instability.

The results of the reactions of hydrazones of aliphatic aldehydes and ketones with mercuric acetate are given in the Table.

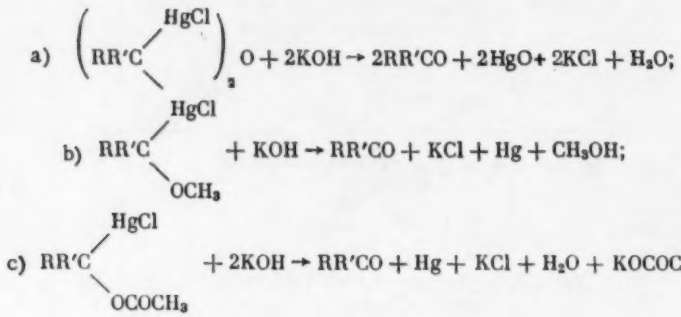
In order to prove the structure of the organomercury compounds formed, they were decomposed with concentrated hydrochloric acid, alkali and bromine. The organomercury compounds of types (I) to (VI) undergo interesting transformations under the action of concentrated hydrochloric acid on heating. Usually organomercury compounds decompose with hydrochloric acid in such a way that the chloromercuri group is substituted by hydrogen, and mercuric chloride is liberated [1]. The organomercury compounds of types (IV-VI) that we obtained from the reactions investigated decomposed with hydrochloric acid with liberation of mercurous chloride and formation of the corresponding carbonyl compounds:

TABLE

Initial hydrazone	Solvent	Organomercury compound formed	Yield in % calc. on hydrazone	Yield in % calc. on mercuric acetate	M.p., (°C)
Acetone hydrazone	Water, Ethanol	α,α',β,β'-Tetra-(chloromercuri)diisopropyl ether 	47	95	150 with decomp.
	Benzene	α,α',β,β'-Tetra-(acetoxymercuri)diisopropyl ether 	96	96	145 with decomp.
Methylethyl ketone hydrazone	Water	α,α',β,β'-Tetra-(chloromercuri)-di-sec.-butyl ether 	9	11	145 with decomp.
	Methanol	2-Methoxy-2,3-di-(chloromercuri)butane 	50	53	130 with decomp.
	Benzene	2-Acetoxy-2,3-di-(chloromercuri)butane 	44	44	147 with decomp.
Butyrone hydrazone	Methanol	4-Methoxy-3,4-di-(chloromercuri)heptane 	42	42	103 with decomp.
	Benzene	Oil	—	—	
	Water	Not examined	—	—	
Acetaldehyde hydrazone	Water	α,α'-Di-(chloromercuri)-diethyl ether 	97	97	75—80
	Methanol	1-Methoxy-1,2-di-(chloromercuri)ethane 	53	75	120—125°
	Benzene	1-Acetoxy-1-(chloromercuri)-ethane 	75	75	Decomposes rapidly

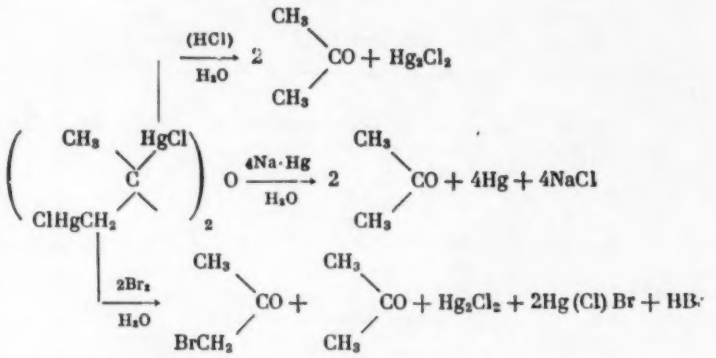


As in the case of haloalkyl-substituted mercury compounds prepared by the aliphatic diazo-compound method [2], the organomercury compounds of types (I-III) decompose with concentrated alcoholic or aqueous alkali with liberation of metallic mercury and formation of the corresponding carbonyl compounds [3]:

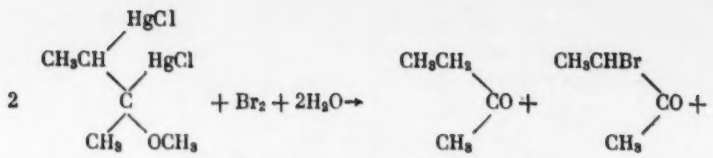


The dimercurated compounds of types (IV-VI) decompose on prolonged heating with alcoholic alkali with liberation of metallic mercury and formation of infusible, polymeric, organomercury compounds which have not been examined further. Bromination of the dimercurated compounds of types (IV-VI) with a solution of bromine in aqueous potassium bromide is a more complex process. In this case the α-bromoketone is formed in addition to the ketone. The position of the halogen in the α-bromoketone formed provides an indication of the position of the second chloromercuri group.

By comparison of these reactions it was possible to establish the structure of the organomercury compounds obtained by reacting acetone and methylethyl ketone hydrazones with mercuric acetate. For example the structure of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether, obtained by reacting acetone hydrazone with mercuric acetate in water, ethanol or absolute benzene was demonstrated by a number of transformations, summarized in the following scheme:



Reduction with sodium amalgam in aqueous medium was undertaken with the object of obtaining diisopropyl ether, thus enabling direct evidence of the presence of the ether grouping in the compound to be obtained. However acetone was formed instead of diisopropyl ether. The structure of 2-methoxy-2,3-di-(chloromercuri)butane obtained by reacting methylethyl ketone hydrazone with mercuric acetate in methanol was proved by decomposition with concentrated hydrochloric acid to mercurous chloride and methylethyl ketone and by bromination, which proceeds according to the equation:



$$+ \mathrm{Hg(Cl)Br} + \mathrm{Hg_2Cl_2} + \mathrm{HCl} + 2\mathrm{CH_3OH}.$$

The position of the bromine in the methyl α-bromoketone indicates the position of the second chloromercuri group. The latter occurs at the α-position in the ethyl radical. The organomercury compounds formed in water and in benzene have similar structures.

In examining the mechanism of the reactions studied, attention should be paid to the following points: a) oxidation of the hydrazones with freshly precipitated yellow mercuric oxide at a temperature of 0-5° in a nonpolar solvent results in the formation of aliphatic diazo compounds according to Equation (4):

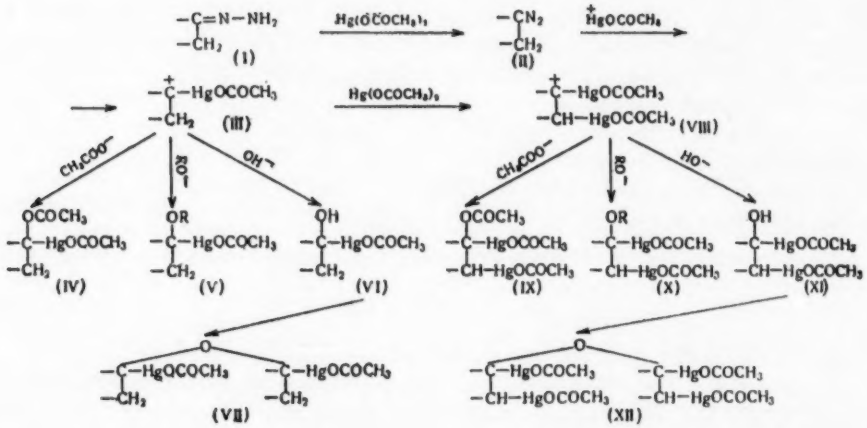
$$RR'C{=}N{-}NH_2 + HgO \rightarrow RR'CN_2 + H_2O + Hg.$$

b) Aliphatic diazo compounds react with mercury halides, arylmercury halides and arylmercury salts of monocarboxylic acids forming α-substituted alkyl mercury derivatives [2]:

$$RR'CN_2 + HgX_2 \rightarrow RR'C(X)HgX + N_2;\ RR'CN_2 + R''HgX \rightarrow RR'C(X)HgR'' + N_2;$$
$$RR'CN_2 + ArHgOCOR'' \rightarrow RR'C(HgAr)OCOR'' + N_2.$$

c) Depending on the nature of the solvent, various reaction products are formed on adding mercury salts to unsaturated compounds [5].

Considering all the above points and taking account of the fact that mercuric acetate, as well as having a reactivity as an oxidizing agent similar to that of mercuric acetate is also able to add depending on the reaction medium, to multiple bonds with the formation of specific types of organomercury compounds, the over-all mechanism of the reactions of hydrazones with mercuric acetate studied can be represented by the following scheme



The hydrazone (I) is oxidized by mercuric acetate to the diazo compound (II). The diazo compound reacts with an acetatomercury cation and by liberating nitrogen forms the mercurated cation (III). Subsequently, depending on structure and the reaction conditions, the cation (III) is stabilized by the addition of an appropriate anion. The addition of an acetoxy group in absolute benzene, an alkoxy group in an alcohol and a hydroxyl group in water results in the formation of the organomercury compounds (IV), (V) and (VI) respectively.

In cation (III) mercury can be substituted for an α-hydrogen atom by the action of mercuric acetate; the dimercurated cation (VIII) combines with the appropriate anion forming the organomercury compounds (IX), (X) and (XI). In water, however, not the organomercury compounds (VI) and (XI) but the di- or tetramercurated ether derivatives (VII) and (XII) are formed.

EXPERIMENTAL

The hydrazones of acetone and methyl ethyl ketone were prepared by the following methods: acetone hydrazone [6] and methyl ethyl ketone hydrazone [7]. The methods of preparation of the hydrazones of acetaldehyde and butyrone are given below.

Acetaldehyde hydrazone. 100 ml (1.77 moles) of freshly distilled acetaldehyde was added dropwise to 105 ml (1.78 moles) of 85% hydrazine hydrate with vigorous stirring and cooling in a mixture of acetone and solid carbon dioxide. On standing for 12 hours the reaction mixture crystallized out as a solid mass. The white, large, prismatic crystals of acetaldehyde hydrazone dihydrate were pressed out, washed with a small quantity of alcohol followed by ether, and dried in the air. Yield, 150 g (88% of theory). Acetaldehyde hydrazone dihydrate is very soluble in water and in alcohol, and insoluble in ether. Melting point after recrystallization from alcohol, 55.5-56°; b.p. 100-103° (745 mm).

Found %: C 25.46; 25.62; H 10.70; 10.61. $C_2H_{10}N_2O_2$. Calculated %: C 25.53; H 10.64.

Butyrone hydrazone. 30 g (0.263 mole) of butyrone was added dropwise with stirring to a mixture of 17 g (0.53 mole) of anhydrous hydrazine (b.p. 113.5°), 30 ml of absolute alcohol and a few granules of BaO, after which the reaction mixture was heated on a boiling water-bath for 4 hours. After cooling, the mixture was filtered and distilled in vacuo. Butyrone hydrazone constituted the fraction of b.p. 75-81° (12 mm); yield, 22.5 g (70% of theory). After repeated redistillation, b.p. 75-80° (12 mm); n_D 1.4619.

Reaction Between Acetone Hydrazone and Mercuric Acetate

α,α',β,β'-Tetra-(chloromercuri)diisopropyl ether. 5 g (0.07 mole) of freshly distilled acetone hydrazone was added dropwise, with vigorous, mechanical stirring to a solution of 44 g (0.14 mole) of mercuric acetate in 250 ml of water, heated to 70°. An exothermic reaction set in immediately with evolution of nitrogen and separation of mercurous acetate. After all the hydrazone had been added the mercurous acetate was completely reduced to metallic mercury. The reaction mixture was then stirred for another 5 minutes, after which the metallic mercury was filtered off. On treating the colorless, aqueous filtrate with 10% KCL solution a white, voluminous, flocculent precipitate of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether separated; yield 17 g of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether – a white, finely crystalline material, soluble in the freshly precipitated and moist state in acetone, alcohol and ammonia; when filtered off and dried it becomes practically insoluble in the usual organic solvents. α,α',β,β'-Tetra-(chloromercuri)diisopropyl ether on standing in an aqueous medium and by the action of concentrated alkali decomposes with separation of metallic mercury, and on heating with concentrated hydrochloric acid, mercurous chloride separates out and acetone is formed. This compound after two reprecipitations with water from acetone solution decomposes above 150° without melting.

Found %: C 7.30; 7.29; H 0.96; 1.09; Hg 76.91; 76.82. $C_6H_{10}Hg_4Cl_4O$. Calculated %: C 6.92; H 0.96; Hg 76.97.

Reaction Between Acetone Hydrazone and Mercuric Acetate in Ethanol

α,α',β,β'-Tetra-(chloromercuri)diisopropyl ether. The reaction was carried out under the same conditions as in water. 17.5 g of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether was obtained from 44 g (0.14 mole) of mercuric acetate, in 250 ml of absolute ethanol, and 5 g (0.07 mole) of acetone hydrazone, after treating the alcoholic filtrate with aqueous KCl solution. The compound obtained corresponded completely in its properties with the α,α',β,β'-tetra-(chloromercuri)diisopropyl ether obtained from water. After two reprecipitations with water from acetone solution the product decomposed above 150° without melting.

Found %: C 7.82; 7.67; H 1.07; 0.99; Hg 76.91; 76.65. $C_6H_{10}Hg_4Cl_4O$. Calculated %: C 6.92; H 0.96; Hg 76.97. $C_5H_{10}Hg_2Cl_2O$. Calculated %: C 10.76; H 1.78; Hg 71.91.

Reaction Between Acetone Hydrazone and Mercuric Acetate in Absolute Benzene

α,α',β,β'-Tetra-(acetoxymercuri)diisopropyl ether. A solution of 5 g (0.07 mole) of acetone hydrazone in 50 ml of absolute benzene was added dropwise, with vigorous mechanical stirring, to a suspension of 88.1 g (0.28 mole) of mercuric acetate in 200 ml of absolute benzene, heated to 70°. Evolution of nitrogen and separation of mercurous acetate began immediately, the reaction mixture rose in temperature and the solution developed a yellow color. After addition of all the hydrazone the reaction mixture was stirred for a further 10 minutes after which the mixture of metallic mercury and mercurous acetate was filtered off. The benzene filtrate was evaporated to constant weight in a current of air. α,α',β,β'-Tetra-(acetoxymercuri)diisopropyl ether remained in the form of a viscous, yellow oil; yield 46 g.

On treatment with ether, alcohol or acetone α,α',β,β'-tetra-(acetoxymercuri)diisopropyl ether becomes crystalline. α,α',β,β'-Tetra-(acetoxymercuri)diisopropyl ether is a yellow, finely crystalline powder, decomposing in alcoholic alkali with liberation of metallic mercury, and in concentrated hydrochloric acid with liberation of mercurous chloride and formation of acetone. This compound dissolves readily in water, dioxane and alcohol, and with difficulty in ether. Decomposition temperature, 145-150° (after reprecipitation with ether from dioxane solution).

Found %: Hg 70.87; 70.95. $C_{14}H_{22}Hg_4O_9$. Calculated %: Hg 70.61.

On treating a dioxane solution of α,α',β,β'-tetra-(acetoxymercuri)diisopropyl ether with 10% KCl solution a white, finely crystalline powder of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether precipitated. The product fully corresponded in properties with α,α',β,β'-tetra-(chloromercuri)diisopropyl ether prepared from acetone hydrazone in water and in ethanol.

Found %: Hg 77.16; 76.86. $C_6H_{10}Hg_4Cl_4O$. Calculated %: Hg 76.97.

Decomposition of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether with bromine in potassium bromide solution. An aqueous solution of bromine, saturated with potassium bromide, was added in small portions in the cold with vigorous agitation, to an aqueous suspension of 35 g of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether. When a considerable excess of bromine had been added, bromoacetone separated in the form of a heavy oil, colored red by the excess bromine. Evolution of gas was observed, resulting from secondary reactions. The reaction was exothermic. After the reaction mixture had been cooled, excess bromine was removed by shaking with saturated sodium thiosulfate solution and the mixture was steam-distilled. The bromoacetone in the distillate was separated from water, dried over fused potassium hydroxide and redistilled in vacuo. The fraction of b.p. 70-80° (40 mm) was collected. According to the literature [8]: b.p. 72-77° (40 mm); yield 3 g (68% of theory). A portion of the bromoacetone was identified in the form of the oxime. Melting point after recrystallization from alcohol, 35-36°. According to the literature [8]: m.p. 36.5°.

On treating of second portion of the bromoacetone obtained with an alcoholic solution of 2,4-dinitrophenylhydrazine in the cold for 24 hours, instead of the expected 2,4-dinitrophenylhydrazone, a compound was obtained that contained no halogen and from analytical data corresponded to the empirical formula $C_{15}H_{14}O_8N_8$. It is probably a compound of the following structure

$$\begin{array}{l} CH_3 - C = N - NH - C_6H_3(NO_2)_2 \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad CH_2 - NH - NH - C_6H_3(NO_2)_2 \end{array}$$

After recrystallization from ethyl acetate the product decomposed above 260° without melting.

Found %: C 41.59; 41.24; H 3.22; 3.16; N 26.04; 25.85. $C_{15}H_{14}O_8N_8$. Calculated %: C 41.49; H 3.22; N 25.80.

The aqueous layer, after separation of the bromoacetone and the fraction boiling below 70° (40 mm), was treated with alcoholic 2,4-dinitrophenylhydrazine solution. A yellow, voluminous precipitate of acetone 2,4-dinitrophenylhydrazone separated. Melting point after recrystallization from alcohol, 122-123°. According to the literature [9], m.p. 122-124°. A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone prepared from acetone gave no depression.

Found %: C 45.54; 45.55; H 4.19; 4.13; N 23.60; 23.75. $C_9H_{10}N_4O_4$. Calculated %: C 45.40; H 4.19; N 23.53.

Decomposition of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether with sodium amalgam in water. 350 g of 2% sodium amalgam was added in small portions with vigorous agitation to an aqueous suspension of 30 g of α,α',β,β'-tetra-(chloromercuri)diisopropyl ether in a flask fitted with a reflux condenser. The reaction mixture was left to stand for a few days, after which metallic mercury and unreacted material was filtered off and the filtrate was distilled. The first 100 ml of distillate was collected. The aqueous distillate was treated with alcoholic 2,4-dinitrophenylhydrazine solution. A voluminous, yellow precipitate of acetone 2,4-dinitrophenylhydrazone separated. Yield, 5 g (74% of theory). Melting point after recrystallization from alcohol, 120-121°. According to the literature [9]: m.p. 122-124°. A mixed melting point with authentic acetone 2,4-dinitrophenylhydrazone gave no depression.

Reaction Between Methylethyl Ketone Hydrazone and Mercuric Acetate

α,α',β,β'-Tetra-(chloromercuri)-di-sec.-butyl ether. 5 g (0.58 mole) of freshly-prepared methylethyl ketone hydrazone was added dropwise with vigorous stirring to a solution of 55.5 g (0.174 mole) of mercuric acetate in 250 ml of water. The reaction was exothermic; nitrogen and mercurous acetate were liberated. After all the hydrazone had been added the reaction mixture was stirred for a few minutes more, then the mercurous acetate was filtered off and the aqueous filtrate was treated with 10% KCl solution. A white, flocculent precipitate of α,α',β,β'-tetra-(chloromercuri)-di-sec.-butyl ether separated; yield, 2.7 g. α,α',β,β'-Tetra-(chloromercuri)-di-sec.-butyl ether is a white finely crystalline material which gradually decomposes in concentrated alcoholic alkali with liberation of metallic mercury. This product dissolves with extreme difficulty in the usual organic solvents. After two precipitations with water from alcoholic solution it decomposes above 145° without melting

Found %: C 9.40; 9.19; H 1.10; 1.15; Hg 75.01; 75.18. $C_8H_{14}Hg_4Cl_4O$. Calculated %: C 8.98; H 1.38; Hg 74.96.

2-Methoxy-2,3-di-(chloromercuri)butane. A solution of 5 g (0.58 mole) of methylethyl ketone hydrazone in 50 ml of methanol was added dropwise, with vigorous stirring, to a refluxing solution of 55.5 g (0.174 mole) of mercuric acetate in 200 ml of methanol. Liberation of nitrogen, mercurous acetate and metallic mercury occurred during the course of the reaction. The alcoholic filtrate was diluted with two volumes of water and treated with 10% KCl solution. A white, flocculent precipitate of 2-methoxy-2,3-di-(chloromercuri)butane separated; yield 12.5 g.

2-Methoxy-2,3-di-(chloromercuri)butane is a white, crystalline substance, stable on storage, which gradually decomposes on heating in dilute alkali with liberation of metallic mercury, and in concentrated hydrochloric acid with formation of methylethyl ketone and mercurous chloride. This product is very soluble in acetone. Melting point after reprecipitation with ether from acetone solution, 130-133° (with decomposition).

Found %: C 11.39; 11.35; H 1.50; 1.60; Hg 72.01; 72.17. $C_5H_{10}Hg_2Cl_2O$. Calculated %: C 10.75; H 1.79; Hg 71.87.

Decomposition of 2-methoxy-2,3-di-(chloromercuri)butane with concentrated hydrochloric acid. 1 g of 2-methoxy-2,3-di-(chloromercuri) butane was refluxed with 20 ml of concentrated hydrochloric acid for 30 minutes. The reaction mixture was diluted to 100 ml with water and filtered from mercurous chloride. The aqueous filtrate was treated with an alcoholic solution of 2,4-dinitrophenylhydrazine and allowed to stand overnight. A yellow, flocculent precipitate of methylethyl ketone 2,4-dinitrophenylhydrazone separated; yield 0.78 g (95% of theory). Melting point after recrystallization from methanol 115-116°. According to the literature [9], m.p. 116-117°. A mixed melting point with authentic methylethyl ketone 2,4-dinitrophenylhydrazone gave no depression.

Decomposition of 2-methoxy-2,3-di-(chloromercuri)butane with bromine in potassium bromide solution. A solution of bromine in potassium bromide was added in small portions, in the cold with vigorous stirring, to a suspension of 5 g (0.009 mole) of 2-methoxy-2,3-di-(chloromercuri)butane in water. A precipitate consisting of a mixture of mercuric and mercurous salts separated immediately. Heavy droplets of methyl- bromoethyl ketone settled at the bottom of the flask. Excess bromine was removed by shaking the reaction mixture with aqueous

sodium thiosulfate solution. The droplets of methyl-α-bromoacetone were separated and the upper layer of the reaction mixture was filtered from the mixture of mercury salts. Yield of crude methyl-α-bromoacetone, 0.8 g (61% of theory).

a) Treatment of methyl-α-bromoacetone. An alcoholic solution of 0.8 g of the ketone was treated with aniline in the cold for 24 hours, the reaction mixture was then filtered from solid impurities and treated with alcoholic semicarbazide hydrochloride. After a few hours crystalline methyl-1-anilinoethyl ketone semicarbazone separated; yield, 0.4 g (36% of theory). Melting point after recrystallization from alcohol, 190°. According to the literature [10], m.p. 190°.

b) Treatment of the aqueous layer. After filtration from the mixture of mercurous and mercuric salts the aqueous layer was treated with alcoholic 2,4-dinitrophenylhydrazine solution. An orange precipitate of methylethyl ketone 2,4-dinitrophenylhydrazone separated immediately; yield, 0.7 g (30% of theory). Melting point after recrystallization from ether, 114-116°. According to the literature [9], m.p. 116-117°. A mixed melting point with authentic methylethyl ketone 2,4-dinitrophenylhydrazone gave no depression.

2-Acetoxy-2,3-di-(chloromercuri)butane. A solution of 5 g (0.058 mole) of methylethyl ketone hydrazone in 50 ml of absolute benzene was added dropwise, with vigorous mechanical stirring to a suspension of 55.5 g (0.174 mole) of mercuric acetate in 200 ml of absolute benzene, heated to 60°. After all the hydrazone had been added the reaction mixture was stirred for a few more minutes, after which the mercurous acetate and metallic mercury were filtered off and the benzene was evaporated to constant weight in a current of air at room temperature. 2-Acetoxy-2,3-di-(acetoxymercuri)butane remained as a viscous, yellow oil; yield, 16 g. 2-Acetoxy-2,3-di-(acetoxymercuri)butane rapidly decomposes on standing in air, with liberation of mercurous acetate and metallic mercury. It was converted to the corresponding chloride by treatment with alcoholic calcium chloride solution.

2-Acetoxy-2,3-di-(chloromercuri)butane is a white, crystalline material, soluble in chloroform, methanol and acetone and insoluble in ether. It decomposes slowly in alcoholic alkali with liberation of metallic mercury, and in concentrated hydrochloric acid with liberation of mercurous chloride. Melting point after two reprecipitations with ether from acetone solution, 147° (with decomposition)

Found %: C 12.27; 12.55; H 1.69; 1.43; Hg 68.54; 68.57. $C_6H_{10}Hg_2Cl_2O_2$. Calculated %: C 12.30; H 1.70; Hg 68.46.

Reaction Between Butyrone Hydrazone and Mercuric Acetate

4-Methoxy-3,4-di-(chloromercuri)heptane. A solution of 5 g (0.039 mole) of freshly-prepared butyrone hydrazone in 50 ml of methanol was added dropwise with vigorous mechanical stirring to a solution of 49.6 g (0.156 mole) of mercuric acetate in 200 ml of methanol, heated to 70°. After the addition of all of the hydrazone, the reaction mixture was stirred for another 10 minutes and then filtered from the mixture of mercurous acetate and metallic mercury. The alcoholic filtrate was carefully treated with 10% aqueous KCl solution. 4-Methoxy-3,4-di-(chloromercuri)heptane precipitated in the form of a heavy oil which crystallized on treatment with ether; yield 10 g. 4-Methoxy-3,4-di-(chloromercuri)heptane is a slightly yellowish, crystalline material that decomposes very slowly in concentrated alcoholic alkali with liberation of metallic mercury, and in concentrated hydrochloric acid with liberation of mercurous chloride and butyrone. Melting point after recrystallization from methanol, 103-108° (with decomposition)

Found %: C 15.86; 15.77; H 2.40; 2.41; Hg 66.70; 66.40. $C_8H_{16}Hg_2Cl_2O$. Calculated %: C 15.99; H 2.66; Hg 66.82.

Reaction Between Acetaldehyde Hydrazone and Mercuric Acetate

α,α'-Di-(chloromercuri)diethyl ether. A solution of 3 g (0.032 mole) of acetaldehyde hydrazone dihydrate in 25 ml of water was added dropwise with vigorous stirring to a solution of 30.4 g (0.095 mole) of mercuric acetate in 250 ml of water, heated to 35-40°. After the addition of all of the hydrazone the reaction mixture was filtered from the mixture of mercurous acetate and metallic mercury. On treatment of the aqueous filtrate with 10% potassium chloride solution a white, flocculent precipitate of α,α'-di-(chloromercuri)diethyl ether separated; yield, 8.5 g. α,α'-Di-(chloromercuri)diethyl ether is a white crystalline material with a very unpleasant odor, soluble in acetone and alcohol and insoluble in ether. This compound decomposes gradually in

daylight, on storing in air and in alcoholic alkali, with liberation of metallic mercury.

Found %: C 8.59; 8.66; H 1.35; 1.45; Hg 73.89; 73.72. $C_4H_8Hg_2Cl_2O$. Calculated %: C 8.82; H 1.47; Hg 73.73.

1-Methoxy-1,2-di-(chloromercuri)ethane. A solution of 5 g (0.053 mole) of acetaldehyde hydrazone dihydrate in 50 ml of methanol was added dropwise, with vigorous stirring, to a solution of 50.8 g (0.16 mole) of mercuric acetate in 200 ml of methanol, heated to 50°. The alcoholic filtrate was diluted with two volumes of water and treated with 10% KCl solution. 1-Methoxy-1,2-di-(chloromercuric)ethane separated as a slightly yellowish, flocculent precipitate with an unpleasant odor; yield, 15 g. This material is soluble in acetone, less soluble in alcohol and insoluble in ether, it decomposes very slowly in alcoholic alkali with liberation of metallic mercury, and in concentrated hydrochloric acid with liberation of mercurous chloride. Melting point after reprecipitation with ether from acetone solution, 120-125°.

Found %: C 7.01; 7.14; H 1.38; 1.40; Hg 75.44; 75.44. $C_3H_6Hg_2Cl_2O$. Calculated %: C 6.80; H 1.13; Hg 75.67.

1-Acetoxy-1-(chloromercuri)ethane. 3 g (0.32 mole) of acetaldehyde hydrazone dihydrate was added to a suspension of 30.4 g (0.095 mole) of mercuric acetate in 250 ml of absolute benzene and the reaction mixture was stirred for 2 hours. Slow evolution of bubbles of nitrogen and separation of a white precipitate of mercurous acetate was observed. The benzene filtrate was evaporated in vacuo at room temperature. 1-Acetoxy-1-(chloromercuri)ethane remained as a viscous, slightly yellowish oil which rapidly decomposed on standing, with liberation of metallic mercury; yield, 5.5 g.

On treatment of the oil with alcoholic calcium chloride solution 1-acetoxy-1-(chloromercuri)ethane was obtained in the form of a slightly yellowish, flocculent solid. This material is soluble in acetone and alcohol, and less soluble in ether, it rapidly decomposes on standing, with liberation of metallic mercury

Found %: Hg 62.08; 62.16. $C_4H_7O_2HgCl$. Calculated %: Hg 62.08.

SUMMARY

1. The reaction of acetaldehyde, acetone, methylethyl ketone and butyrone hydrazones with mercuric acetate provides a method of preparation of some new types of organomercury compounds.

2. This reaction is of the "conjugated addition" type with the medium taking part. In water, α,α'-dimercurated or α,α',β,β'-tetramercurated ethers are formed, in methanol – α-mercurated or α,β-dimercurated alkylmethyl ethers, and finally in absolute benzene – α-mercurated or α,β-dimercurated alkyl acetates.

3. The chemical properties of the organomercury compounds obtained have been studied and it was shown that: a) the dimercurated compounds of types (IV-VI) decompose on heating with concentrated hydrochloric acid with liberation of mercurous chloride and formation of the corresponding carbonyl compound; b) bromination of dimercurated compounds of types (IV-VI) with bromine and saturated aqueous potassium bromide solution in the cold leads to the formation of the corresponding α-bromoketone in addition to the ketone; c) the monomercurated compounds of types (I-III) decompose in concentrated alkali in the cold with liberation of metallic mercury and formation of the corresponding carbonyl compound.

M. V. Lomonosov Moscow State University

Received March 20, 1957

LITERATURE CITED

[1] R. Adams, F. L. Roman and W. N. Sperry, J. Amer. Chem. Soc. 44, 1791 (1922).

[2] L. Hellerman and D. Newman, J. Amer. Chem. Soc. 54, 2859 (1932); A. N. Nesmeianov and G. Povkh, J. Gen. Chem. 4, 958 (1934); R. Kh. Freidlina and A. N. Nesmeianov, Proc. Acad. Sci. USSR, 26, 59 (1940); R. Kh. Freidlina, A. N. Nesmeianov and F. L. Tokareva, J. Gen. Chem., 7, 262 (1937); A. N. Nesmeianov, A. Borisov and A. Abramova, Bull. Acad. Sci., Div. Chem. Sci. 1946, 647; P. Pfeifer and H. Jäger, Ber. 80, 1 (1947); P. Pfeifer, R. Schulze-Bentrop, K. H. La Roche and E. Schmitz, Ber. 85, 232 (1952).

[3] A. N. Nesmeianov, O. A. Reutov and A. S. Loseva, Proc. Acad. Sci. USSR, 111, 835 (1956).*

[4] T. Curtius, and K. Thun, J. prakt. chem. 44, 161 (1891); T. Curtius and H. Lang, J. prakt. chem. 44, 544 (1891); T. Curtius and F. Rauterberg, J. prakt. chem. 44, 192 (1891); H. Staudinger, and A. Gaule, Ber. 49, 1897 (1916); H. Staudinger and O. Cupfer, Ber. 44, 2197 (1911); H. Staudinger, G. Goldstein, Ber. 49, 1923 (1916); H. Staudinger, A. Anthes and F. Pfenninger, Ber. 49, 1928, 1941 (1916).

[5] L. G. Makarova and A. N. Nesmeianov, Synthetic Methods in the Field of Organometallic Compounds of Mercury, Acad. Sci. USSR Press, Moscow-Leningrad, 1945, p. 53 [in Russian].

[6] T. Curtius and L. Pflug, J. prakt. chem. 44, 535 (1891).

[7] A. Kirrman, Comptes rend, 217, 148 (1943).

[8] R. Scholl and G. Mattaiopoulos, Ber. 29, 1556 (1896).

[9] W. Dirscherl and H. Nahm, Ber. 73B, 448 (1940).

[10] J. R. Catch, D. F. Elliot, D. H. Hey, and E. R. H. Jones, J. Chem. Soc. 1948, 272.

*Original Russian pagination. See C. B. Translation.

THE PROBLEM OF THE STEREOCHEMISTRY OF THE REACTION OF SYMMETRICAL ORGANOMERCURY COMPOUNDS WITH MERCURIC HALIDES

A. N. Nesmeianov, O. A. Reutov, Wu Yang-Ch'ieh and Lu Ching-Chu

In a study of the stereochemistry of the symmetrization reaction of the diastereomeric L-menthyl α-bromomercuriphenylacetates (I) and (II) [(I) $-[\alpha]^{18}D = -90°$; (II) $-[\alpha]^{18}D = -49°$] with ammonia in chloroform it was found [1] that from the diastereomer (I) a single isomer of a symmetrical organomercury compound of $[\alpha]^{18}D$ −2° is formed, and also from the diastereomer (II) a single isomer of a symmetrical compound of $[\alpha]^{18}D$ −8°.

It follows from these results that symmetrization of the organomercury salts (I) and (II), which is an electrophilic substitution reaction, proceeds with retention of the stereochemical configuration

$$R_1R_2R_3C-HgBr + R_1R_2R_3C-Hg-Br \xrightarrow{2NH_3} R_1R_2R_3C-Hg-CR_1R_2R_3 + HgBr_2\cdot(NH_3)_2$$

($R_1 = C_6H_5$; $R_2 = H$; $R_3 = COOC_{10}H_{19}$)

at the saturated carbon atom of (I). This conclusion is supported also by the fact that the action of an equimolar quantity of alcoholic hydrogen bromide on the symmetrical compound of $[\alpha]^{18}D$ −2°, obtained by the symmetrization of (I) leads to the formation of pure (I), free from (II).

$$C_6H_5-CH(HgBr)-COOC_{10}H_{19} \xrightarrow{NH_3} C_6H_5-CH(Hg-CH(C_6H_5)-COOC_{10}H_{19})-COOC_{10}H_{19} \xrightarrow{HBr}$$

$[\alpha]^{18}_D - 86°$ $\qquad$ $[\alpha]^{18}_D - 2°$

$$\longrightarrow C_6H_5-CH(HgBr)-COOC_{10}H_{19} + C_6H_5-CH_2-COOC_{10}H_{19}$$

$[\alpha]^{18}_D$ −86°

A study of the kinetics of symmetrization has shown [2] that this reaction is a two-stage process. The role of ammonia is confirmed

a) $2R_1R_2R_3C-HgBr \rightleftarrows (R_1R_2R_3C)_2Hg + HgBr_2$;

b) $HgBr_2 + 2NH_3 \rightarrow HgBr_2\cdot(NH_3)_2$.

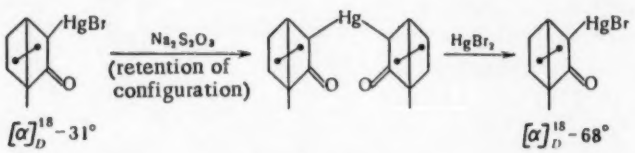
to combination with the mercuric bromide, as a result of which the equilibrium of (a) is shifted to the right.

Since organomercury diastereomers $R_1R_2R_3C-HgBr$ do not racemize in solution in organic solvents on standing in the cold, it follows from the existence of the equilibrium (a) that both the forward (symmetrization) reaction and the reverse reaction (reaction between the symmetrical compound and mercuric bromide) must take place with retention of configuration. The reaction of the symmetrical compound of $[\alpha]^{18}D$ −2° and that of the symmetrical compound of $[\alpha]^{18}D$ −8° with mercuric bromide at the boiling point of acetone results in the formation of an equimolar mixture of the diastereomeric L-menthyl α-bromomercuriphenylacetates (I) and (II). On the basis of this we put forward the hypothesis [1] that this reaction takes place with inversion of the stereochemical configuration. However, on further investigation of this reaction we found that the formation of a mixture of diastereomers is brought about by secondary racemization which accompanies the main reaction under these conditions. The secondary racemization can be eliminated by carrying out the reaction at room temperature. Thus, on reacting equimolar quantities of mercuric bromide and the menthyl α-bromomercuribisphenylacetate of $[\alpha]^{18}D$ −2°, obtained by symmetrization of the pure diastereomer (I), the latter was formed in acetone solution in the cold during the course of a week:

$$\begin{array}{l} C_6H_5-CH-COOC_{10}H_{19} \\ \quad\quad | \\ \quad\quad Hg \\ \quad\quad | \\ C_6H_5-CH-COOC_{10}H_{19} \\ \quad [\alpha]_D^{18}\ -2^\circ \end{array} \xrightarrow{HgBr_2} 2C_6H_5-CH(HgBr)-COOC_{10}H_{19},\quad [\alpha]_D^{18}\ -86^\circ$$

Hence in contrast to our previous hypothesis [1] we conclude that the reaction between the symmetrical α-mercurated L-menthyl phenylacetate and mercuric bromide, which is an electrophilic substitution process at a saturated carbon atom, takes place with retention of the stereochemical configuration at this carbon atom, as does the symmetrization reaction under the action of ammonia.* It should be noted that mercuric bromide slowly racemizes the α-bromomercuriphenylacetic ester in acetone solution in the cold. Consequently elimination of secondary racemization of the product formed on reacting the symmetrical compound with mercuric bromide is possible only because the symmetrical compound reacts considerably more rapidly with $HgBr_2$ than does the unsymmetrical compound.

Such a marked difference in the reactivity of symmetrical organomercury compounds and the corresponding organomercury salts does not always occur. Thus, for example, it is evidently not so marked in the case of mercuribis-α,α'-camphor and 3-bromomercuricamphor. On reacting mercuribiscamphor, obtained by symmetrization with sodium thiosulfate of the pure diastereomer, 3-bromomercuricamphor** of $[\alpha]^{18}D$ −31° (symmetrization takes place with preservation of the configuration), with mercuric bromide in acetone solution, even in the cold, a mixture of diastereomers of $[\alpha]^{18}D$ −68° is formed. Evidently the formation of a molecule of 3-bromomercuricamphor of inverse configuration of the α-carbon atom must be connected with secondary racemization (of the



$[\alpha]_D^{18}$ −31° $[\alpha]_D^{18}$ −68°

3-bromomercuricamphor of $[\alpha]^{18}D$ −31°, formed initially) by the action of mercuric bromide. In this case the racemization probably proceeds at a rate comparable with that of the main reaction — the reaction between mercuribiscamphor and mercuric bromide. This fact prevents elucidation of the actual stereochemistry of the electrophilic substitution at the carbon atom from the example of the reaction of mercuribis-α,α'-camphor with mercuric bromide.

---

* Winstein and co-workers [3] have shown by means of radioactive mercury that the reaction of cis-2-methoxycyclohexylneophylmercury with mercuric chloride takes place with retention of stereochemical configuration at the carbon atom of the cyclohexane ring which is involved in the reaction.

** L-3-Bromomercuricamphor exists in the form of two diastereomers (I) and (II) of $[\alpha]^{18}$ −31°, m. p. 222-223° and $[\alpha]^{18}D$ −126°, m.p. 216-218° respectively.

EXPERIMENTAL*

1. Reaction of the diastereomeric, symmetrical, α-mercurated L-menthyl phenylacetate with an equimolar quantity of hydrogen bromide. 0.45 g ($6.05 \cdot 10^{-4}$ mole) of symmetrical α-mercurated L-menthyl phenylacetate of $[\alpha]^{18}D$ −2° and m.p. 123°, obtained by symmetrization of the pure diastereomer, L-menthyl α-bromomercuriphenylacetate of $[\alpha]^{18}D$ −86° and m.p. 153° with ammonia, was dissolved in 50 ml of absolute chloroform. 5 ml of alcoholic hydrogen bromide solution containing 0.054 g of HBr ($6.65 \cdot 10^{-4}$ mole) was added dropwise to this solution over a period of one hour, with vigorous stirring. The mixture was stirred for a further hour and then evaporated to dryness in the cold in a current of air. The dry residue was washed with alcohol. The yield of L-menthyl α-bromomercuriphenylacetate was 0.28 g (84% of theory).

After recrystallization from alcohol,** m.p. 153-154°, $[\alpha]^{18}$ −86° ± 2° (c = 0.55; l = 1.9; $\alpha_D = -0.9° \pm 0.03°$). Yield of product, 0.22 g (77% of theory).

2. Reaction of the diastereomeric, symmetrical, α-mercurated L-menthyl phenylacetate with mercuric bromide. 0.21 g (2.8×10^{-4} mole) of symmetrical α-mercurated L-menthyl phenylacetate of $[\alpha]^{18}D$ −2° and m.p. 123°, obtained by symmetrization of the pure diastereomer, L-menthyl α-bromomercuriphenylacetate of $[\alpha]^{18}D$ −86° and m.p. 153°, and 0.089 g ($2.5 \cdot 10^{-4}$ mole) of mercuric bromide were dissolved in 60 ml of absolute acetone. The reaction mixture was allowed to stand in the cold and the residue was washed with hot water; yield 0.275 g. After crystallization from carbon tetrachloride,*** m.p. 152-153° and $[\alpha]^{18}D$ −86° ± 2° (c = = 0.563; l = 1.9; α_D = −0.93° ± 0.03°). Yield 0.22 g (71% of theory).

3. "Racemization" of L-menthyl α-bromomercuriphenylacetate by the action of mercuric bromide. 0.53 g ($7 \cdot 10^{-4}$ mole) of the pure stereoisomer, L-menthyl α-bromomercuriphenylacetate ($[\alpha]^{18}D$ −86°; m.p. 153°), and 0.35 g ($9.7 \cdot 10^{-4}$ mole) of mercuric bromide were dissolved in 100 ml of absolute acetone. The reaction mixture was allowed to stand in the cold for a week. The acetone was then evaporated in the cold and the residue washed with hot water until the washings were free from mercuric bromide (test with alkali). The residue weighed 0.49 g after washing. The product was dissolved by heating in carbon tetrachloride and a few drops of methyl alcohol were added to the solution, which was then cooled to −10°. On rubbing the sides of the vessel a precipitate of L-menthyl α-bromomercuriphenylacetate separated; yield 0.28 g; $[\alpha]^{18}D$ −74° ± 2° (c = 0.562; l = 1.9; $\alpha_D = -0.80 \pm 0.03°$).

4. Reaction of mercuribis-α,α'-camphor with mercuric bromide. 0.52 g (0.001 mole) of unrecrystallized**** mercuribis-α,α'-camphor, prepared by symmetrization with sodium thiosulfate of the pure diastereomer, 3-bromomercuricamphor, of $[\alpha]^{18}D$ −30°, and 0.36 g (0.001 mole) of mercuric bromide were dissolved in 100 ml of absolute acetone. The reaction mixture was allowed to stand in the cold for a week. The acetone was evaporated in the cold and the residue was washed with hot water. After drying in a vacuum desiccator over calcium chloride the 3-bromomercuricamphor obtained weighed 0.8 g (91% of theory); m.p. 218-220°; $[\alpha]^{18}D$ −64° ± 1.5° (c = 1.9; l = 1.9; $\alpha_D = -2.3° \pm 0.05°$).

5. "Racemization" of 3-bromomercuricamphor by the action of mercuric bromide. 0.43 g (0.001 mole) of the pure diastereomer, 3-bromomercuricamphor of $[\alpha]^{18}D$ −30°, and 0.36 g (0.001 mole) of mercuric bromide were dissolved in 400 ml of absolute acetone. The reaction mixture was allowed to stand in the cold for a week. The acetone was then evaporated in the cold and the residue was washed with hot water until the washings were free from mercuric bromide (test with alkali). After drying in a vacuum desiccator over calcium chloride the yield of 3-bromomercuricamphor was 0.4 g; m.p. 218-220° $[\alpha]^{18}D$ −68° ± 1.5° (c = 1.8; l = 1.9; $\alpha_D = -2.3° \pm 0.05°$).

---

*In order to test reproducibility all experiments were carried out 2-3 times.

**Recrystallization under these conditions (solution of the material in alcohol by heating, cooling the solution to −10° and rubbing the sides of the beaker with a glass rod) of 0.3 g of a mixture of the diastereomers of L-menthyl α-bromomercuriphenylacetate of $[\alpha]^{18}D$ −76° did not lead to the separation of this mixture. The recrystallized product weighed 0.24 g and had $[\alpha]^{18}D$ −77°.

***Recrystallization under these conditions of a mixture of the diastereomeric menthyl bromomercuriphenylacetates did bring about its separation.

****Symmetrization of 3-bromomercuricamphor with sodium thiosulfate takes place with retention of configuration at the α-carbon atom [4]. On crystallization of the mercuribiscamphor obtained, partial racemization of the configuration at the α-carbon atom sets in.

SUMMARY

1. The stereochemistry of the reactions of symmetrical, α-mercurated L-menthyl phenylacetate and mercuribis-α,α'-camphor with mercuric bromide in acetone solution has been studied. Both reactions are examples of electrophilic substitution at a saturated carbon atom.

2. It is shown that the first reaction proceeds with retention of configuration at the carbon atom in question. The racemization observed at 56° is a secondary process.

3. It is not possible to elucidate the stereochemistry of the reaction between mercuribis-α,α'-camphor and mercuric acetate because the 3-bromomercuricamphor formed racemizes even in the cold by the action of mercuric acetate under the experimental conditions.

4. By a study of the reaction of the symmetrical, α-mercurated L-menthyl ester with an equimolar quantity of hydrogen bromide the conclusion, drawn previously [1], that the symmetrization of organomercury salts proceeds with retention of the configuration at the saturated carbon atom was confirmed.

M. V. Lomonosov Moscow State University

Received March 20, 1957

LITERATURE CITED

[1] A. N. Nesmeianov, O. A. Reutov and S. S. Poddubnaia, Proc. Acad. Sci. USSR 88, 479 (1953); Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 850.*

[2] O. A. Reutov, I. P. Beletskaia and R. E. Mardaleishvili, Proc. Acad. Sci. USSR 116, No. 4, 617 (1957).*

[3] S. Winstein, T. G. Traylor and C. S. Garner, J. Amer. Chem. Soc. 77, 3741 (1955).

[4] O. A. Reutov and Lu Ching-Chu, Proc. Acad. Sci. USSR 110, 575 (1956).*

*Original Russian pagination. See C. B. Translation.

ESTERS OF PHOSPHORIC AND THIOPHOSPHORIC ACIDS CONTAINING HETEROCYCLIC RADICALS

COMMUNICATION 1. COMPOUNDS WITH PYRIMIDYL AND IMIDOMETHYLURACIL RADICALS

A. Arbuzov and V. M. Zoroastrova

Among the organic derivatives of phosphorus, the attention of research workers has recently been directed more and more toward compounds containing heterocyclic groupings within their structure complex. Interest in these compounds has arisen mainly because some of them (esters of phosphinic, phosphoric and thiophosphoric acids) possess biological activity. Thus, for example, 2-isopropyl-4-methyl-6-pyrimidylethyl thiophosphate is known, under the name Diazinon, as a powerful insecticide with a wide range of activity and of low toxicity to warm-blooded animals [1]. It was therefore of some interest to study other representatives of this type of compound and to subject them to biological tests.

We have synthesized a number of phosphoric and thiophosphoric esters with pyrimidyl and imidouracil radicals. The physical properties of the compounds prepared are given in Table 1.

TABLE 1

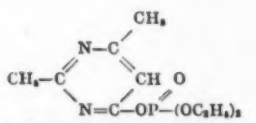
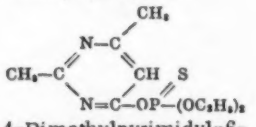
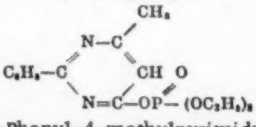
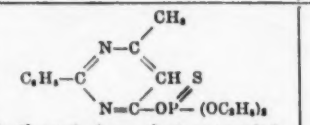
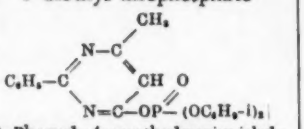
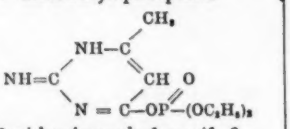
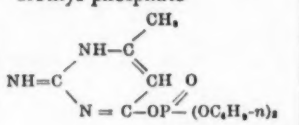
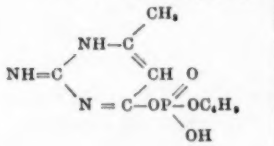
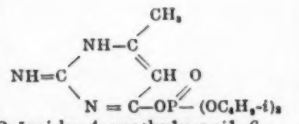
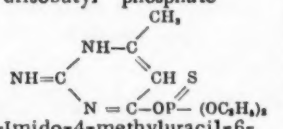
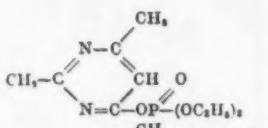
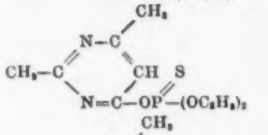
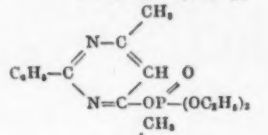
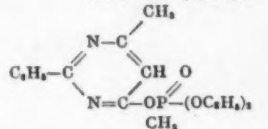
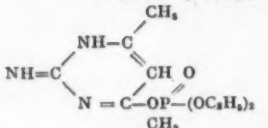
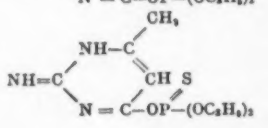
Number	Formula and name of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_0^{20}	MR found	MR calculated	Yield in %	Notes
1	 2,4-Dimethylpyrimidyl-6-diethyl phosphate	153—157 (5,5)	1,4720	1,1561	63,00	63,62	18	From Ag salt
2	 2,4-Dimethylpyrimidyl-6-diethyl thiophosphate	152—154 (4)	1,5060	1,1507	71,30	69,21	28	The same
		93—95 (0,13) [2]	1,5010	1,1455	71,03	69,21	25	
3	 2-Phenyl-4-methylpyrimidyl-6-diethyl phosphate	M.p. 69—70°					50	
							78,3	From Na salt

TABLE 1 (continued)

Number	Formula and name of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_0^{20}	RM found	RM calculated	Yield in %	Notes
4	 2-Phenyl-4-methylpyrimidyl-6-diethyl thiophosphate	M.p. 46—48 180—182 (3,5—4)	1,5433	1,1470	90,24	89,80	70	The same
5	 2-Phenyl-4-methylpyrimidyl-6-diisobutyl phosphate	M.p. 64—65					72,6	"
6	 2-Imido-4-methyluracil-6-diethyl phosphate	M.p. 110—111					51,6	From Ag salt
7		M.p. 106—107					57,8	The same
		84—85 (0,02)	1,4290	0,9837	68,43			
8	 2-Imido-4-methyluracil-6-diisobutyl phosphate	M.p. 114—116					54,7	"
9	 2-Imido-4-methyluracil-6-diethyl thiophosphate	M.p. 107—108					57	"

Compounds No. 1 and 2 are high-boiling, viscous, oily liquids, readily soluble in the usual organic solvents and to a lesser extent in water. Compound No. 2 was described by Shvetsova-Shilovskaia, Mel'nikov and Grapov [2]. The physical constants found by us are close to those reported in the literature. Compound No. 4 was isolated both in the liquid (which could not be made to crystallize) and in the crystalline states. All the remaining compounds containing pyrimidyl radicals are solid materials of relatively low melting point.

TABLE 2

No.	Formula of compound	Concentration in %	Mortality in %	Toxicity
1		0,005 0,05 0,01	66 (7 days) 100 (15 hrs) 100 (5 days)	Compound of low toxicity
2		0,005 0,05	100 (6 days) 100 (after 2 days)	"
3		0,01 0,05 0,1	34 (7 days) 100 (8 ") 99 (7 ") 100 (3 ")	LD_{100}—15 mg/kg
4		0,005 0,05 0,1	64 (10 days) 50 100 (up to 7 days) 100 (up to 7 days)	
5		0,05 0,01	100 (after 1 day) 80 (after 5 days)	LD_{100}—2,5 mg/kg
6		0,05 0,01	100 (2 days) 64 (after 7 days)	LD_{100}—16 mg/kg

We synthesized the compounds containing pyrimidyl radicals through either the sodium or silver salts of the pyrimidines. Products No. 3, 4 and 5 were prepared in good yield from the sodium salt of 2-phenyl-4-methyl-6-hydroxypyrimidine. This method proved to be very suitable because it involves heating the reactants for a shorter time than in the case of the silver salt and, moreover, the products obtained from the sodium salt were purer than those from the silver salt. In the latter case they were contaminated with colloidal silver halide which made them difficult to purify.

The compounds with imidouracil radicals could not be prepared through the sodium salt under our experimental conditions; we prepared them by reacting the silver salt with the dialkylphosphoryl chloride in dry toluene or xylene with yields of 51.6-57.8%. These compounds are crystalline materials of relatively low melting point, good solubility in the usual organic solvents and poorer solubility in water. It was characteristic of all the compounds (both with pyrimidyl and with imidouracil radicals) that the water solubility of those containing ethyl radicals was greater than in the case of the n- and isobutyl analogs.

In addition we attempted to prepare the n-butyl ester (No. 7) by the method described by Shvetsova-Shilovskaia, Mel'nikov and Grapov [2] from imidomethyluracil and di-n-butylphosphoryl chloride in the presence of potassium hydroxide. However, we obtained a product corresponding by analysis to the imidomethylbutyl acid ester of phosphoric acid.

We hydrolyzed some of the esters prepared. On hydrolysis with hydrochloric acid (1:1) the parent pyrimidine or imidomethyluracil is obtained normally.

Repeated experiments on the preparation of phosphoric and thiophosphoric esters from the sodium salts of other uracils, namely: 4-methyluracil and thio-4-methyluracil, did not give positive results. In no case could any individual product be isolated from the reaction mixture apart from large amounts of the original uracils and resinous products. We did not carry out synthesis through the Ag salts of 4-methyluracil and thio-4-methyluracil because the salts themselves were not obtained in the pure state.

Some of the compounds synthesized were tested by M. A. Kudrina in the Kazan branch of the Academy of Sciences USSR for insecticide activity with respect to the long-nosed granary weevil, and for toxicity to mice. The results obtained are given in Table 2.

EXPERIMENTAL

2,4-Dimethyl-6-hydroxypyrimidine was prepared by condensing acetamidine hydrochloride with ethyl acetoacetate [3], m.p. 194-195°. The sodium salt of 2,4-dimethyl-6-hydroxypyrimidine was prepared by dissolving the latter in the theoretical quantity of aqueous sodium hydroxide solution and evaporating the solution to dryness. The salt was finally dried at 130-135° in a drying oven, for 4 hours. The silver salt of 2,4-dimethyl-6-hydroxypyrimidine was prepared by the action of silver nitrate on a solution of the pyrimidine in aqueous ammonia.

2-Phenyl-4-methyl-6-hydroxypyrimidine was prepared, like the dimethylhydroxypyrimidine, by reacting equimolar quantities of benzamidine hydrochloride and ethyl acetoacetate in the presence of a small amount of 10% alkali solution. After recrystallization from toluene the product melted at 215-216.5°. The sodium salt of 2-phenyl-4-methyl-6-hydroxypyrimidine was prepared by the action of an equimolar quantity of sodium hydroxide on the hydroxypyrimidine. The salt was dried at 130-135° for 6 hours or in vacuo (12-15 mm) in toluene vapor for 2 hours. The silver salt of 2-phenyl-4-methyl-6-hydroxypyrimidine was prepared according to the method of Pinner [4].

Preparation of 2,4-Dimethylpyrimidyl-6-diethyl Phosphate

a) Reaction of the silver salt of 2,4-dimethyl-6-hydroxypyrimidine with diethylphosphoryl chloride. 23.09 g of the silver salt of 2,4-dimethyl-6-hydroxypyrimidine, 17.25 g of diethylphosphoryl chloride and 100 ml of dry toluene were heated for 6 hours under reflux with mechanical stirring. At the end of the reaction the silver halide was filtered off and washed a few times with toluene. After removal of the solvent the reaction products were distilled several times in vacuo. Among other fractions, boiling over a wide range of temperature, two products were isolated: Fraction I, b.p. 65-67° (5 mm); 2.4 g; $n^{20}D$ 1.4780; d^{20}_0 1.0141, a liquid with an amine-like odor. Contained only a trace of phosphorus. Composition and structure were not determined.

Fraction II, b.p. 153-157° (5.5 mm) (with slight decomposition); 3.7 g (18% of theory); $n^{20}D$ 1.4720; d^{20}_0 1.1561; calculated MR 63.62; found MR 63.00. This product is a viscous, slightly yellow liquid with a faint odor; soluble in benzene, ether, alcohol and water.

Found %: P 12.24. $C_{10}H_{17}O_4N_2P$. Calculated %: P 11.92.

b) Reaction of the sodium salt of 2,4-dimethyl-6-hydroxypyrimidine with diethylphosphoryl chloride. 10.83 g of the sodium salt of 2,4-dimethyl-6-hydroxypyrimidine and 13 g of diethylphosphoryl chloride (1 mole to 1 mole of salt) in 50 ml of dry xylene were refluxed, with mechanical stirring, for 2 hours. The reaction mixture consisted of a dark-brown liquid with a colloidal suspension of sodium chloride and residual pyrimidine salt. After removal of the solid material by centrifuging, the liquid portion was distilled in vacuo. 2 g of product of b.p. 147-150° (4-4.5 mm); $n^{20}D$ 1.4875; d^{20}_0 1.1348, was isolated.

A large quantity of resinous material remained in the distillation flask.

Found %: P 8.29; $C_{10}H_{17}O_4N_2P$. Calculated %: P 11.52.

From the analytical data the product is the impure pyrimidyl phosphoric ester.

Preparation of 2,4-Dimethylpyrimidyl-6-diethyl Phosphate

9.8 g of diethylphosphoryl chloride was added to 12 g of the silver salt of 2,4-dimethyl-6-hydroxypyrimidine in 50 ml of dry xylene. The temperature of the mixture rose from 20 to 28°. The mixture was stirred and heated for 6 hours. Silver chloride (8.3 g) was filtered off at the end of the reaction. The filtrate was a liquid of the color of strong tea. After two distillations in vacuo from an Arbuzov flask, a yellow, rather viscous liquid with an odor typical of sulfur compounds was obtained; yield 4.02 g, 28% of theory; b.p. 152-154° (4 mm); $n^{20}D$ 1.5060; d^{20}_0 1.1507; found MR 71.30; calculated MR 69.21. The product was readily soluble in the usual organic solvents and poorly soluble in water (better in hot water).

Found %: P 10.78; S 11.51. $C_{10}H_{17}O_3N_2SP$. Calculated %: P 11.22; S 11.61.

Preparation of 2-Phenyl-4-methylpyrimidyl-6-diethyl Phosphate

a) From the silver salt. 18 g of the Ag salt and 11 g of diethylphosphoryl chloride (1 mole to 1 mole) in 70 ml of dry toluene were refluxed, with mechanical stirring, for 10 hours. The silver halide precipitate was filtered from the hot mixture. On cooling, small needles of 2-phenyl-4-methyl-6-hydroxypyrimidine separated from the filtrate (2 g); m.p. 212-215°. The toluene was evaporated by heating on the water bath under slightly reduced pressure. Petroleum ether was added to the residual, viscous, crude material. On rubbing with a glass rod the whole mass solidified. 10 g, or 50% of theory, of crude product was obtained. The product was recrystallized three times from petroleum ether. The compound obtained consisted of colorless needles of m.p. 69-70°, readily soluble in alcohol, ether, benzene, acetone, ethyl acetate and other solvents; poorly soluble in cold water.

Found %: P 9.71; 9.56. $C_{15}H_{19}O_4N_2P$. Calculated %: P 9.62.

Hydrolysis of product: 0.2 g of the substance of m.p. 69-70°, and 7 ml of HCl (1 : 1) were refluxed for 2 hours. The contents of the flask were evaporated on the water bath with continuous addition of water until all the hydrogen chloride had been removed. The dry residue was recrystallized from hot water after treatment with activated charcoal. Crystalline 2-phenyl-4-methyl-6-hydroxypyrimidine of m.p. 215-216° was obtained.

b) From the sodium salt. The sodium salt of 2-phenyl-4-methyl-6-hydroxypyrimidine (5.2 g) was added to 4.31 g of the hydrochloride dissolved in 35 ml of dry xylene. Almost all the salt soon went into solution with an increase in temperature from 19 to 43°. A turbid solution was formed reminiscent of a liquid, starch paste. The mixture was refluxed and stirred for 1.5 hours. The colloidal precipitate of sodium chloride was separated by centrifuging. The xylene was removed under slightly reduced pressure. The crystalline material that separated was filtered off and washed with petroleum ether. Yield of crude product, 6.5 g or 78.3% of theory. Large, thin needles melting at 69-71° were obtained by recrystallization from petroleum ether. A mixture with the product obtained from the silver salt of 2-phenyl-4-methyl-6-hydroxypyrimidine and diethylphosphoryl chloride melted at 69-70.5°.

Preparation of 2-Phenyl-4-methylpyrimidyl-6-diethylthiophosphate

a) From the silver salt of 2-phenyl-4-methyl-6-hydroxypyrimidine. Diethylthiophosphoryl chloride (5.59 g) was added in one lot to 8.7 g of the silver salt in 45 ml of dry toluene. A small increase in temperature from 21 to 28° was observed. The mixture was refluxed for 6 hours. After cooling, the silver chloride was filtered off. The filtrate was worked up in two ways.

A portion of the reaction product was redistilled in vacuo. A small fraction of b.p. 180-182° (3.5-4 mm) (with decomposition) was separated – a viscous, oily, yellow liquid with an unpleasant odor: $n^{20}D$ 1.5433; d^{20}_0 1.1470; found MR 90.24; calculated MR 89.80.

A large residue remained in the flask in the form of a viscous, red resin.

Found %: P 9.54; 9.74. $C_{15}H_{19}O_3SN_2P$. Calculated %: P 9.16.

Hydrolysis of the liquid product: 0.1 g of the product was heated in a sealed tube for 6 hours with 5 ml of HCl (1 : 1) at 120-125°. Crystalline 2-phenyl-4-methyl-6-hydroxypyrimidine of m.p. 213-215° was obtained.

The toluene was distilled under slightly reduced pressure from the other portion of the filtrate. The residue in the flask solidified on rubbing with a glass rod to a white mass melting at 40-45° and readily soluble in many organic solvents. The product melted at 46-48° after recrystallization from petroleum ether and consisted of colorless crystals of low solubility in cold, and better solubility in hot, water.

Found %: P 9.66. $C_{15}H_{19}O_3SN_2P$. Calculated %: P. 9.16.

Hydrolysis of the crystalline product: 0.3 g of the product was heated in a sealed tube at 120-135° for 6 hours with 15 ml of HCl (1 : 1). On evaporation of the solution on the water bath, crystals of a faint, dull pink color and m.p. 213-215° were obtained; after recrystallization from alcohol with activated charcoal they melted at 215-216.5° (the parent 2-phenyl-4-methyl-6-hydroxypyrimidine).

b) From the sodium salt of 2-phenyl-4-methyl-6-hydroxypyrimidine. 6 g of the sodium salt of 2-phenyl-4-methyl-6-hydroxypyrimidine and 5.4 g of diethylthiophosphoryl chloride in 40 ml of dry xylene was heated and stirred for 1.5 hours. At the end of the reaction the colloidal precipitate of sodium chloride was separated by

centrifuging. The solvent was distilled off in vacuo at 30-35 mm. The crude residue crystallized out on adding petroleum ether and rubbing with a glass rod. 5 g of crude product (70% of theory) was filtered off. The product was recrystallized several times from petroleum ether; m.p. 46-48°.

Found %: P 9.49; 9.41. $C_{15}H_{19}O_3SN_2P$. Calculated %: P 9.16.

Preparation of 2-Phenyl-4-methylpyrimidyl-6-diisobutyl Phosphate

2-Phenyl-4-methylpyrimidyl-6-diisobutyl phosphate was prepared from the Na salt and the hydrochloride similarly to the previous compound. 2.5 g of Na salt, 2.6 g of diisobutylphosphoryl chloride and 20 ml of dry xylene were taken. The mixture was refluxed and stirred for 0.5 hours. 3.3 g (72.6% of theory) of crude product was obtained. After recrystallization from petroleum ether (thin needles) or water (small prisms) the product melted at 64-65°. The product was similar in properties to the compound containing the ethyl radical.

Found %: P 8.55; 8.55. $C_{19}H_{27}N_2O_4P$. Calculated %: P 8.19.

Hydrolysis of the product of m.p. 64-65°. A small quantity of the product was refluxed for 5 hours with 5 ml of HCl (1:1). The solution was evaporated on the water bath with several additions of water until the HCl was removed. Crystals of the parent pyrimidine of m.p. 213-215.5° were obtained. Mixed melting point with pure material, 214-215.5°.

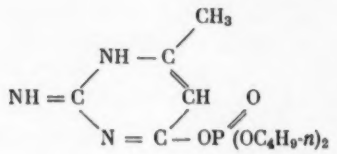
Preparation of 2-Imido-4-methyluracil-6-diethyl Phosphate

The silver salt of imidomethyluracil was prepared by precipitation from a hot, aqueous solution of imidomethyluracil with a hot NH_4OH solution of silver nitrate. The precipitate was washed well with water and with alcohol, and dried first at 100°, and then at 130° for 3 hours.

8.1 g of the silver salt of imidomethyluracil and 6 g of diethylphosphoryl chloride were refluxed, with mechanical stirring, for 30 minutes in 80 ml of dry xylene. The colloidal precipitate of silver chloride was filtered from the hot mixture, 4.7 g (51.6% of theory) of crystalline material, of m.p. 97-103°, precipitated from the filtrate after removal of a large proportion of the xylene. The product was recrystallized from a mixture of benzene and petroleum ether (activated charcoal). Well-formed, colorless prisms of m.p. 110-111° were obtained, readily soluble in organic solvents and in hot water.

Found %: P 12.19; 12.23. $C_9H_{16}O_4N_3P$. Calculated %: P 11.87.

Hydrolysis of the product of m.p. 110-111°. 0.2 g of the product was refluxed for 3 hours in 10 ml of HCl (1:1). The aqueous solution was evaporated on the water bath until all the hydrogen chloride was removed. Crystals of imidomethyluracil of m.p. ~290° (with decomposition) were obtained.

Preparation of 

Experiment 1. In contrast to the previous experiment the reaction was carried out in toluene solution. A mixture of 6.96 g of the silver salt of imidomethyluracil and 6.87 g of di-n-butylphosphoryl chloride in 50 ml of dry toluene was refluxed, with stirring, for 0.5 hours. After separation of silver chloride the filtrate was evaporated in vacuo. Thin needles contaminated with silver halide were obtained. Yield 5.5 g or 57.8% of theory. The product was recrystallized a few times from a mixture of benzene and petroleum ether. Fibrous, colorless crystals of m.p. 106-107° were obtained.

Found %: P 9.84; 9.98. $C_{13}H_{24}O_4N_3P$. Calculated %: P 9.77.

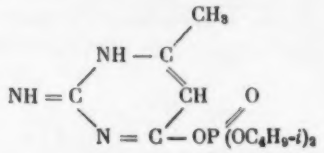
Hydrolysis of the product. 0.1 g of the product of m.p. 106-107° was refluxed with 5 ml of HCl (1:1) for 5 hours. A solid product was obtained that darkened on heating to 260° (impure imidomethyluracil).

Experiment 2. A mixture of 7.2 g of imidomethyluracil and 7.55 g of potash (potassium hydroxide?) was refluxed in 80 ml of dry toluene for 2 hours. The water was distilled off with the toluene. 13.16 g of di-n-butylphosphoryl chloride and 30 ml of dry toluene were added to the residue. The mixture was refluxed for 27 hours. 25-30 ml of water was added at the end of the reaction. The toluene layer was separated from the aqueous layer, which consisted of a pasty mass. The two layers were worked up separately. The aqueous layer was extracted a few times with benzene but after removal of the benzene there was practically no residue in the flask (only 2 g of the original imidomethyluracil was isolated). A product was isolated from the toluene solution, first by molecular distillation and then by ordinary distillation in high vacuum. 2.7 g of material boiling at 84-85° (0.02 mm); $n^{20}D$ 1.4290, d^{20}_0 0.9837, was obtained.

Found %: P 11.85; 11.58. $C_9H_{16}O_4PN_3$. Calculated %: P 11.88.

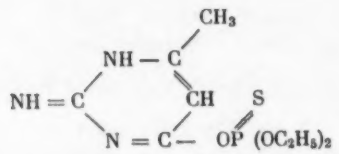
Found %: M 255; 254.8. $C_9H_{16}O_4PN_3$. Calculated %: M 261.12.

Hence from the analytical data the product is close to the acid ester.

Preparation of 

The diisobutyl ester was prepared from the silver salt of imidomethyluracil (3.46 g) and diisobutylphosphoryl chloride (3.4 g) in xylene solution. 2.7 g (54.7% of theory) of crude product was isolated. The product melted at 114-116° after recrystallization from petroleum ether; very fine needles, similar in properties to the analogous n-butyl ester.

Found %: P 10.06. $C_{13}H_{24}O_4N_3P$. Calculated %: P 9.77.

Preparation of 

2.5 g of the silver salt of imidomethyluracil and 1.9 g of diethylthiophosphoryl chloride were refluxed for 15 minutes in 20 ml of dry xylene. The contents of the flask rapidly developed a dark-gray color (silver halide). The precipitate of silver chloride was filtered off and the filtrate was allowed to stand in a large beaker. After a few minutes a precipitate separated (1.7 g –57%), which was recrystallized twice from benzene and petroleum ether. The product was a colorless, crystalline material of m.p. 107-108°. It was soluble in alcohol, ether, benzene, acetone, chloroform and other organic solvents. It was soluble also in hot water.

Found %: S 11.72. $C_9H_{16}O_3SPN_3$. Calculated %: S 11.57.

SUMMARY

A number of esters of phosphoric and thiophosphoric acids, containing pyrimidyl and imidouracil radicals, have been synthesized and studied.

A. M. Butlerov Chemical Institute
V. I. Ul'ianov-Lenin Kazan State University

Received March 21, 1957

LITERATURE CITED

[1] R. Gasser (J. R. Geigy, L. – C. Basal, Switz); Z. Naturforsch. 8b, 225 (1953); Chem. Abstrs. 10167 (1953).

[2] K. D. Shvetsova-Shilovskaia, N. N. Mel'nikov and A. F. Grapov, J. Gen. Chem. 3, 808 (1956).*

[3] A. Pinner, Ber. 17, 2520 (1884).

[4] A. Pinner, Ber. 18, 2848 (1885).

*Original Russian pagination. See C. B. Translation.

THE SYNTHESIS OF SOME ESTERS OF α-(DIALKYLPHOSPHONYL)-β,β,β-TRICHLOROETHYLPHOSPHORIC ACIDS AND α-(DIALKYLPHOSPHONYL)-β,β,β-TRICHLOROETHYL ESTERS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES

K. V. Nikonorov

In the past 2-3 years the attention of Russian and foreign chemists has been directed toward the study of the reaction between chloral and dialkyl- and trialkyl phosphites. By this reaction ester of α-hydroxy-β,β,β-trichloroethylphosphinic and β,β-dichlorovinylphosphoric acids have been prepared [1]. In the present work an attempt was made to bring about a reaction between the dimethyl (I) and diethyl (II) esters of α-hydroxy-β,β,β-trichloroethylphosphoric acid and various dialkylphosphoryl chlorides and some carboxylic acids.

The starting compounds (I) and (II) were prepared by the method of Barthel and co-workers [2]. Synthesis of the esters of α-(dialkyphosphonyl)-β,β,β-trichloroethylphosphoric acids was achieved by reacting various dialkylphosphoryl chlorides with (I) and (II) in the presence of triethylamine, according to the equation:

$$(RO)_2P(O)CH(OH)CCl_3 + ClP(O)(OR)_2 + Et_3N \rightarrow (RO)_2P(O)CH(OP(O)(OR)_2)CCl_3 + Et_3N.HCl$$

The reaction takes place sluggishly, without marked evolution of heat and is completed by 10-12 hours at room temperature.

The α-(dialkylphosphonyl)-β,β,β-trichloroethyl carboxylic acid esters and some of their derivatives were prepared by the action of carboxylic acid chlorides on (I) and (II) also in the presence of triethylamine:

$$(RO)_2P(O)CH(OH)CCl_3 + ClCOR' + Et_3N \rightarrow (RO)_2P(O)CH(OCOR')CCl_3 + Et_3N.HCl,$$

where R' = CH_3; C_2H_5; C_3H_7-n, C_3H_7-i; $CH_3CH(Br)$; $N(C_2H_5)_2$. As would be expected, this reaction proceeds more vigorously; it is accompanied by marked evolution of heat and is completed in 2-3 hours. The constants of the compounds obtained are given in Tables 1 and 2. The esters indicated in Tables 1 and 2 are rather mobile, colorless liquids with a faint odor.

In view of the fact that the parent compounds, particularly (I), are powerful insecticides [3], the esters synthesized by us were also examined in this connection. Preliminary tests, carried out at the Kazan branch of the Academy of Sciences USSR by M. A. Kudrina, showed that all the compounds obtained possess fairly powerful insecticidal properties. Investigations carried out in the Scientific Institute of Fertilizers and Insectofungicides by E. A. Pokrovskii established the existence of a systemic activity in this type of compound against some forms of biting insects.

TABLE 1

Esters of α-(Dialkylphosphonyl)-β,β,β-trichloroethyl Phosphoric Acids

No.	Formula of ester	Yield, in %	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	P content in % found	P content in % calculated
1	$(CH_3O)_2P(O)CHCl_2OP(O)(OCH_3)_2$	35,2	118—120 (0,05)	1,4592	1,4798	67,55	67,38	16,55; 16,65	16,9
2	$(CH_3O)_2P(O)CHCl_2OP(O)(OC_2H_5)_2$	33,5	119—121 (0,05)	1,4590	1,4128	76,138	76,51	16,15; 15,82	15,8
3	$(CH_3O)_2P(O)CHCl_2OP(O)(OC_3H_7)_2$	50,5	120—122 (0,02)	1,4506	1,3228	85,73	85,74	14,7; 14,6	14,7
4	$(CH_3O)_2P(O)CHCl_2OP(O)(OC_3H_7\text{-}i)_2$	41,5	116—117 (0,05)	1,4340	1,2880	85,62	85,74	15,1; 15,1	14,7
5	$(CH_3O)_2P(O)CHCl_2OP(O)(OC_4H_9)_2$	32,0	132—133 (0,05)	1,4515	1,2608	96,08	95,18	14,2; 14,1	13,8
6	$(CH_3O)_2P(O)CHCl_2OP(O)(OC_4H_9\text{-}i)_2$	52,5	129—131 (0,02)	1,4608	1,3047	94,5	95,18	13,6; 13,6	13,8
7	$(C_2H_5O)_2P(O)CHCl_2OP(O)(OC_2H_5)_2$	63,1	126—128 (0,05)	1,4642	1,3551	85,86	85,75	14,42; 14,52	14,7
8	$(C_2H_5O)_2P(O)CHCl_2OP(O)(OC_3H_7)_2$	58,2	139—140 (0,02)	1,4580	1,2904	95,03	94,98	14,1; 13,9	13,8
9	$(C_2H_5O)_2P(O)CHCl_2OP(O)(OC_3H_7\text{-}i)_2$	57,0	129—131 (0,02)	1,4606	1,3040	95,54	94,98	13,6; 13,7	13,8
10	$(C_2H_5O)_2P(O)CHCl_2OP(O)(OC_4H_9)_2$	66,6	145—148 (0,02)	1,4422	1,2140	104,22	104,32	13,2; 13,1	13,0
11	$(C_2H_5O)_2P(O)CHCl_2OP(O)(OC_4H_9\text{-}i)_2$	53,5	140—142 (0,05)	1,4635	1,2657	104,0	104,32	12,9 —	13,0
12	$(C_2H_5O)_2P(O)CHCl_2OP(S)(OC_2H_5)_2$	41,1	136—139 (0,02)	1,4572	1,3036	90,95	91,03	14,1; 14,1	14,2

TABLE 2

α-(Dialkylphosphonyl)-β,β,β-trichloroethyl Esters of Carboxylic Acids and Some of Their Derivatives

No.	Formula of ester	Yield, in %	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated
1	$(CH_3O)_2PCHOCOCH_3$ ‖ O CCl$_3$	80,8	83—84 (0,03)	1,4730	1,4724	57,06	57,03
2	$(CH_3O)_2PCHOCOC_2H_5$ ‖ O CCl$_3$	72,5	92—93 (0,015)	1,4730	1,4251	61,71	61,65
3	$(CH_3O)_2PCHOCOC_3H_7$ ‖ O CCl$_3$	65,0	112—114 (0,03)	1,4740	1,3998	65,75	66,26
4	$(CH_3O)_2PCHOCOCH(CH_3)_2$ ‖ O CCl$_3$	64,5	110—112 (0,05)	1,4725	1,3957	65,77	66,26
5	$(CH_3O)_2P$ CHOCOCHCH$_3$ ‖ | | O CCl$_3$ Br	59,0	130—131 (0,04)	1,4925	1,6290	69,96	69,41
6	$(C_2H_5O)_2P$ CHOCOCH$_3$ ‖ | O CCl$_3$	70,0	90—93 (0,027)	1,4650	1,3631	66,42	66,27
7	$(C_2H_5O)_2P$ CHOCOC$_2$H$_5$ ‖ | O CCl$_3$	72,5	96—97 (0.03)	1,4658	1,3269	71,25	70,88
8	$(C_2H_5O)_2P$ CHOCOC$_3$H$_7$ ‖ | O CCl$_3$	75,0	124—125 (0,05)	1,4685	1,3141	72,27	75,50
9	$(C_2H_5O)_2P$ CHOCOCH(CH$_3$)$_2$ ‖ | O CCl$_3$	58,0	115—119 (0,02)	1,4660	1,3033	75,55	75,50
10	$(C_2H_5O)_2P$ CHOCOCHCH$_3$ ‖ | | O CCl$_3$ Br	66,2	136—137 (0,05)	1,4846	1,5074	79,89	79,65
11	$(C_2H_5O)_2P$ CHOCON(C$_2$H$_5$)$_2$ ‖ | O CCl$_3$	44,2 (0,04)	120—121 (0,04)	1,4740	1,2964	84,00	83,974

EXPERIMENTAL

Preparation of dialkyl esters of α-(dialkylphosphonyl)-β,β,β-trichloroethylphosphoric acids. Triethylamine and the calculated quantity of the dialkylphosphoryl chloride was added to (I) or (II) dissolved in diethyl ether or in a mixture of diethyl ether and a small quantity of benzene. The reaction proceeded slowly without appreciable evolution of heat, and required stirring at room temperature for 10-12 hours for its completion. At the end of the reaction triethylamine hydrochloride was filtered off, the diethyl ether was distilled off and the residue was distilled in vacuo. In a number of cases the crude reaction product prior to normal vacuum distillation was subjected to film-type molecular distillation. This distillation was carried out in a simple film-type molecular still [4] at 0.015-0.02 mm. Thus, for example, diethyl α-(dimethylphosphonyl)-β,β,β-trichloroethylphosphate was prepared from 10 g (0.039 mole) of (I), 4.3 g (0.042 mole) of triethylamine and 6.7 g (0.039 mole of diethylphosphoryl chloride in 70 ml of diethyl ether. Two distillations in vacuo from an Arbuzov flask yielded 5.15 g (33.5% of theory) of pure material (No. 2, Table 1) of b.p. 119-121° (0.05 mm); $n^{20}D$ 1.4590; d^{20}_4 1.4128; found MR 76.13; calculated MR 76.51.

Found %: P 16.15; 15.82. $C_8H_{17}O_7Cl_3P_2$. Calculated %: P 15.8.

All the remaining 11 compounds indicated in Table 1 were prepared under similar conditions.

Preparation of α-(dialkylphosphonyl)-β,β,β-trichloroethyl esters of carbosylic acids and some of their derivatives. Triethylamine was added to (I) or (II) dissolved in diethyl ether or a mixture of diethyl ether and a small quantity of benzene, and the calculated quantity of the acyl halide was added dropwise, with stirring. The reaction was slightly exothermic and was completed in 2-3 hours. At the end of the reaction triethylamine hydrochloride was filtered off, the diethyl ether was distilled off and the residue was distilled in vacuo. Thus, for example, α-(dimethylphosphonyl)-β,β,β-trichloroethyl acetate was prepared from 8 g (0.031 mole) of (I), 3.2 g (0.031 mole) of triethylamine and 2.44 g (0.031 mole) of acetyl chloride in 50 ml of diethyl ether and 10 ml of

TABLE 2 (continued)

P content in %		C content in %		H content in %		Cl content in %	
found	calculated	found	calculated	found	calculated	found	calculated
10,20; 10,0	10,03	24,40; 23,66	24,0	3,36; 3,35	3,34	— —	—
9,80; 9,89	9,87	27,15; 27,05	26,8	3,99; 3,9	3,83	34,1; 34,4	34,0
9,86; 9,80	9,9	— —	—	— —	—	— —	—
10,03; 9,92	9,52	— —	—	— —	—	— —	—
8,32; 8,35	7,9	— —	—	— —	—	— —	—
9,72; 9,71	9,47	29,30; 29,30	29,4	4,30; 4,40	4,27	32,8; 32,8	32,5
9,4; 9,2	9,1	31,7; 31,8	31,6	4,77; 4,8	4,68	31,2; 31,4	31,15
9,28; 9,45	8,72	— —	—	— —	—	— —	—
9,18; 9,3	8,72	— —	—	— —	—	— —	—
8,18; 8,25	7,4	25,58; 25,14	25,65	3,68; 3,80	3,57	— —	—
8,51; 9,45	8,05	34,40; 34,25	34,44	5,50; 5,40	5,45	— —	—

benzene. Distillation in vacuo from an Arbuzov flask yielded 7.55 g (80.8% of theory) of pure material of b.p. 83-84° (0.03 mm); $n^{20}D$ 1.4730; d^{20}_4 1.4724; found MR 57.06; calculated MR 57.03.

Found %: C 23.40; 23.66; H 3.36; 3.35; P 10.20; 10.00. $C_6H_{10}O_5Cl_3P$. Calculated %: C 24.0; H 3.34; P 10.03.

The remaining 10 compounds indicated in Table 2 were prepared by similar means. When bases other than triethylamine are used, for example pyridine, the reaction proceeds more slowly.

SUMMARY

1. Various esters of α-(dialkylphosphonyl)-β,β,β-trichloroethylphosphoric acid have been prepared by reacting the dimethyl and diethyl esters of α-hydroxy-β,β,β-trichloroethylphosphoric acid with dialkylphosphoryl chlorides in the presence of triethylamine.

2. α-(Dialkylphosphonyl)-β,β,β-trichloroethyl esters of carboxylic acids and some of their derivatives have been prepared in good yields by reacting the dimethyl and diethyl esters of α-hydroxy-β,β,β-trichloroethylphosphoric acid with acyl halides.

3. The compounds synthesized possess insecticidal activity.

A. E. Arbuzov Chemical Institute
Kazan Branch Acad. Sci. USSR

Received March 18, 1957

LITERATURE CITED

[1] W. Perkow, Chem. Ber. 87, 755 (1954); A. E. Arbuzov and P. I. Alimov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 530.

[2] W. F. Barthel, P. A. Giang and S. A. Hall, J. Amer. Chem. Soc. 76, 4186 (1954).

[3] W. F. Barthel, B. H. Alexander, P. A. Giang and S. A. Hall, J. Amer. Chem. Soc. 77, 2424 (1955).

[4] A. Ia. Berlin, Technique of Laboratory Work in Organic Chemistry, State Chem. Press, Moscow 1952, p. 115.

REACTIONS OF FLUOROOLEFINS

COMMUNICATION 8. REACTIONS OF PERFLUOROVINYLMAGNESIUM HALIDES

I. L. Knuniants, R. N. Sterlin, R. D. Iatsenko and L. N. Pinkina

Prior to 1946, attempts to prepare organomagnesium derivatives of completely halogenated hydrocarbons were unsuccessful [1]. In 1946, Brice [2] described the interaction of C_3F_7Br with magnesium; in his opinion, the reaction proceeded with the formation of C_3F_7MgBr. The only proof of the formation of an organomagnesium derivative was the formation of a small amount of C_3F_7H when the reaction mixture was decomposed with acid, although the reaction conditions did not exclude the formation of this product by the interaction of C_3F_7Br with the solvent.

The systematic investigation of methods of preparation and of the properties of perfluoroalkylmagnesium halides was begun in 1952 by Haszeldine and co-workers [3]. As a result of more than 300 experiments, they were able to show that the major conditions determining the successful formation of C_3F_7MgBr are the use of spectroscopically pure magnesium, activation of the magnesium with iodine and alkyl bromides, the use of electron-donor solvents as the reaction medium, and low temperatures (−50 to 0°). The yield of C_3F_7MgI was as high as 80% when the indicated conditions were observed. Haszeldine also showed that CF_3I can react with magnesium with the formation of CF_3MgI, but the reaction rate is approximately 1000 times less in this case. Both C_3F_7MgI and CF_3MgI were reacted with carbon dioxide, aldehydes, ketones, esters, and acid chlorides, and these reactions led to products analogous to those which are formed in the ordinary Grignard synthesis. In 1956, Park showed that perfluorovinyl iodide in ether solution can react with magnesium (activated with iodide) at 0° with the formation of $CF_2=CFMgI$ in 50% yield. The only proof of the formation of this compound was similar to the proof offered by Brice, conversion of trifluoroethylene by treatment of the reaction mixture with acid.

We have now shown that by activating the magnesium with ethyl bromide and carrying out the reaction in ether at −30 to −20°, it is possible to obtain practically quantitative consumption of the magnesium. By treating the reaction mixture with dilute acid, we were able to obtain a 70% yield of trifluoroethylene.

It was also shown that perfluorovinyl bromide and perfluorovinyl chloride do not react with magnesium under these conditions, and are recovered from the reaction mixture unchanged. It was possible to react perfluorovinyl bromide with magnesium to form the organomagnesium compound if the reaction was carried out in tetrahydrofuran; the yield of $CF_2=CFMgBr$ was 45%. Furthermore, it was not even necessary to activate the magnesium with ethyl bromide. Apparently, the assertion [5] that an increase in the basicity of the solvent promotes the formation of R_FMgI at the expense of stabilization of the compound in the form of a complex of the type $\begin{matrix} R_2O \\ \downarrow \\ R_FMgI \\ \uparrow \\ R_2O \end{matrix}$, is correct.

In order to prove that a new type of organomagnesium compound was formed, we carried out a reaction between $CF_2=CFMgI$ and carbon dioxide.

Treatment of $CF_2=CFMgI$ in ether solution at −40° with solid carbon dioxide and subsequent decomposition of the reaction mixture with 2 N sulfuric acid resulted in a 40% yield of perfluoroacrylic acid, which had previously been synthesized only by an extremely complex multistage route by Henne [6]. This method for the preparation

of perfluoroacrylic acid is recommended as a preparative procedure. Treatment of an ether solution of perfluoroacrylic acid with the calculated amount of diazomethane yields the methyl ester of perfluoroacrylic acid.

EXPERIMENTAL*

Preparation of perfluorovinylmagnesium bromide. The experiment was carried out in a four-neck flask fitted with a stirrer, a thermometer, a diffuser for the introduction of the $CF_2=CFBr$, and an outlet tube connected to a Tishchenko bottle containing H_2SO_4. 13 g of $CF_2=CFBr$ was fed (from a pressure bomb through the diffuser) to the flask which contained 4 g of iodine-activated magnesium and 100 ml of tetrahydrofuran at −20 to −25°. The mixture was then stirred for an hour, after which it was transferred to another flask which had been purged with nitrogen and cooled to −25°. The residual magnesium was washed with two portions of tetrahydrofuran of 10 ml each. The solution of $CF_2=CFMgBr$ was cooled to −20°, and 50 ml of 2 N H_2SO_4 was added with vigorous stirring. The gas evolved was collected in traps at −110°; 1.9 ml of trifluoroethylene was collected, all of which distilled at −56°. Literature data [7]: b.p., −56°; found mol. wt., 82.92 and 80.48; calculated mol. wt., 82.0. This $CF_2=CFH$ was converted to the dibromide, $CF_2Br-CFHBr$, with a b.p. of 76-76.5°; $n^{18}D$ 1.4125. Literature data [8]: b.p. 76-76.5°; $n^{14}D$ 1.41447; the yield of $CH_2=CFH$ and, consequently, of $CF_2=CFMgBr$ was 43.3%.

Preparation of perfluorovinylmagnesium iodide. In a four-neck flask fitted with a stirrer, a dropping funnel, a thermometer, and an outlet tube connected to a Tishchenko bottle containing H_2SO_4 were placed 5 g of magnesium (shavings) and several crystals of iodine which had been sublimed over P_2O_5. The system was purged with dry nitrogen, and the flask was mildly heated to sublime the iodine; the flask was then cooled, and 30 ml of absolute ether and 2 g of C_2H_5Br were introduced. Just as the violent reaction began, the ether solution was decanted, and the residual magnesium was repeatedly washed with ether to remove the C_2H_5MgBr. 70 ml of ether was then introduced into the flask, the system was again purged with nitrogen, and the reaction mixture was cooled to −20°. 19.25 g of $CF_2=CFI$ was added to the flask with vigorous stirring; the temperature inside the flask was maintained at −20 to −5° by means of external cooling. Stirring was continued for another hour after addition of the $CF_2=CFI$ was complete; the ether solution was decanted from the remaining magnesium (2.58 g of Mg reacted) into another, similar reaction flask, the magnesium was carefully washed with ether, and this ether solution was added to the main solution. The resulting ether solution of $CF_2=CFMgI$ was stirred vigorously, and 2 N H_2SO_4 was added to decompose the perfluorovinylmagnesium iodide. The gas evolved was collected in traps at −110°. A total of 6.5 g of gas was collected. When distilled in a Podbielniak column, all of the gas came overhead at −56°. According to the literature, the boiling point of trifluoroethylene is −56° [8]. The yield of $CF_2=CFH$ and, consequently, of $CF_2=CFMgI$ was 69%.

Preparation of perfluoroacrylic acid. Solid carbon dioxide was added over a period of 8 hours to an ether solution of $CF_2=CFMgI$ (prepared from 21 g of $CF_2=CFI$ and 2.8 g of Mg); the addition was carried out at a temperature of −70 to −40°. The reaction mixture was allowed to stand overnight at a temperature of −80°; on the following day, carbon dioxide was added for another 5 hours. The reaction mixture was heated to 20° and treated with 150 ml of 2 N H_2SO_4. The ether layer was separated, and the aqueous layer was extracted 15 times with 10-15 ml portions of ether. The combined ether solutions were dried over $MgSO_4$, and were then agitated with mercury. The ether was distilled, and the residue was sublimed under vacuum. 4.8 g of perfluoroacrylic acid, m.p. 36°, was obtained; the yield was 37.7%; mol. wt. found, 127.3 and 126.5; mol. wt. calculated for $C_3HO_2F_3$, 126.

Found %: F 44.5; 44.2. $C_3HO_2F_3$. Calculated %: F 45.2.

Preparation of the methyl ester of perfluoroacrylic acid. 4.77 g of perfluoroacrylic acid in 15 ml of ether was treated, with stirring, with an ether solution of diazomethane (1.7 g of CH_2N_2 in 50 ml of ether) at −12°. After the evolution of nitrogen (0.6 liter) had ceased and the reaction mixture had acquired a slightly yellow color, the addition of diazomethane was stopped, and the mixture was allowed to stand overnight. The ether solution was dried over $MgSO_4$, and the ether was distilled; distillation of the residue gave 2.7 g of a substance with a b.p. of 84-86° (0.5 g of kettle residue). A second distillation gave a fraction with a b.p. of 84-85°; this fraction, which had a sharp, irritating odor, was the methyl ester of perfluoroacrylic acid; the yield was 58%; $n^{21.5}D$ 1.3590; $d^{21.5}_4$ 1.3259; found MR, 23.22; MR calculated, 22.16; mol. wt. found, 135.0 and 138.0; mol. wt. calculated for $C_4H_3O_2F_3$, 140.0.

* V. L. Isaev participated in the work.

Found %: C 34.55; 34.42; H 2.14; 2.14; F 39.8; 39.01. $C_4H_3O_2F_3$. Calculated %: C 34.29; H 2.14; F 40.6.

SUMMARY

1. It was shown that perfluorovinylmagnesium iodide and perfluorovinylmagnesium bromide can be prepared in yields of 70 and 45%, respectively, in a reaction medium of ether or tetrahydrofuran.

2. A new method was found for the preparation of perfluoroacrylic acid; the method comprises the reaction of $CF_2=CFMgI$ with carbon dioxide.

Received March 4, 1957

LITERATURE CITED

[1] F. Runge, Organomagnesium Compounds, ONTI, 1937.*

[2] T. Brice et al., J. Amer. Chem. Soc. 68, 968 (1946).

[3] R. Haszeldine et al., J. Chem. Soc. 1952, 3423; 1953, 1748; 1954, 1273.

[4] J. Park et al., J. Amer. Chem. Soc. 78, 59 (1956).

[5] R. Haszeldine, J. Chem. Soc. 1952, 3423.

[6] A. Henne and C. Foche, J. Amer. Chem. Soc. 76, 479 (1954).

[7] F. Swarts, Bull. Acad. roy. Belgique 34, 307 (1897).

[8] J. Park et al., J. Amer. Chem. Soc. 78, 711 (1951).

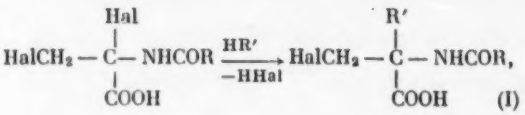
*Russian translation.

α,β-DISUBSTITUTED α-ACYLAMINOCARBOXYLIC ACIDS*

COMMUNICATION 2. A NEW METHOD OF PREPARING OXAZOLE-4-CARBOXYLIC ACIDS

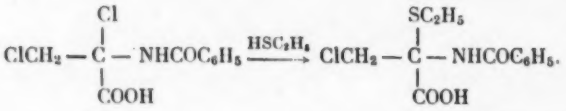
O. V. Kil'disheva, M. G. Lin'kova, V. M. Savosina and I. L. Knuniants

It was reported previously [1] that α,β-dihalo-α-acylaminopropionic acids readily react with water, alcohols, and amines with the formation of α-substituted α-acylamino-β-halocarboxylic acids (I)



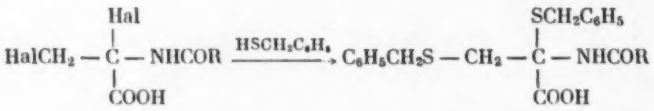
where R' is OH, OAlk, or NHAr.

Further investigation has shown that α,β-dihalo-α-acylaminopropionic acids readily react with mercaptans to yield, depending on the halogen (chlorine or bromine), mono- or dialkylthio acids. Thus, the action of one mole of ethyl mercaptan on α,β-dichloro-α-benzamidopropionic acid yields α-ethylthio-α-benzamido-β-chloropropionic acid (II) with an m.p. of 114°.



(II)

With benzyl mercaptan and at any reactant ratio, both α,β-dichloro- and α,β-dibromo-α-acylaminopropionic acids (III) form only α,β-dialkarylthio-α-acylaminopripionic acids (IV).



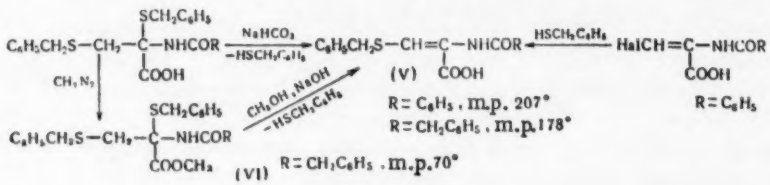
(III) (IV)

R = C_6H_5; m.p. 131°

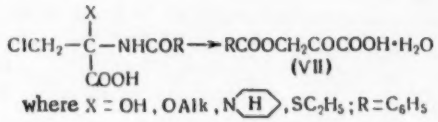
R = $CH_2C_6H_5$; m.p. 170—171°.

*See [1] for Communication 1.

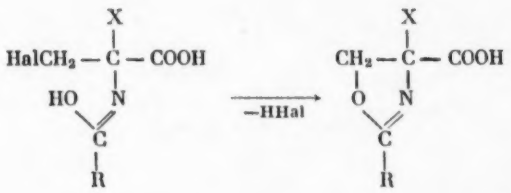
Investigation of the properties of the resulting dialkarylthio acids showed that they are rather unstable, and evan their reprecipitation from bicarbonate solutions with acids is accompanied by loss of a considerable amount of benzyl mercaptan with the formation of β-benzylthio-α-acylaminoacrylic acids (V) as by-products: these acids are identical to the corresponding acids obtained by the interaction of benzyl mercaptan with β-halo-α-acylamino-acrylic acids [2].



The corresponding methyl esters are readily obtained by the action of diazomethane on α,β-dialkylthio-α-acylaminopropionic acids (VI). Saponification of the esters with alcoholic NaOH also led to the formation of β-benzylthio-α-acylaminoacrylic acid (V). However, when reprecipitated by acid from bicarbonate solution, α-ethylthio-α-benzamido-β-chloropropionic acid, $ClCH_2-\underset{\underset{COOH}{|}}{\overset{\overset{SC_2H_5}{|}}{C}}-NHCOC_6H_5$, described above, is converted to a considerable extent to benzoyloxypyruvic acid (VII), which has previously been prepared from other α-substituted α-acylamino-β-halocarboxylic acids [3].

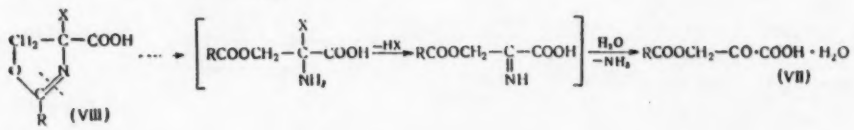


The mechanism of the formation of acyloxypyruvic acids from α-substituted α-acylamino-β-halocarboxylic acids has previously been demonstrated by us [3]. Owing to the presence of a halogen atom in the β-position, these acids are very easily converted to 2-alkaryl- or 2-aryloxazoline-4-carboxylic acids (VIII) having a substituent X in the 4-position of the oxazoline ring.

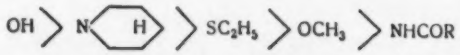


(VIII)

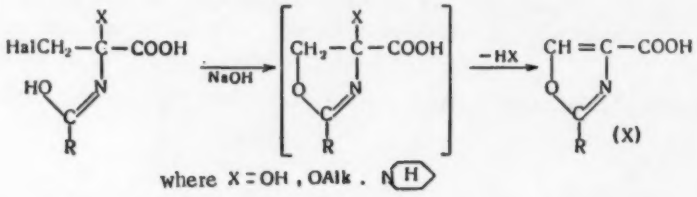
Oxazolinecarboxylic acids are generally readily decomposed by acids; the presence of a substituent X in the 4-position makes them still more unstable, and they readily decompose in acid solution with the formation of the still more unstable β-acyloxy-α-amino-α-substituted propionic acids (IX); the latter readily lose HX and then ammonia with the formation of acyloxypyruvic acids.



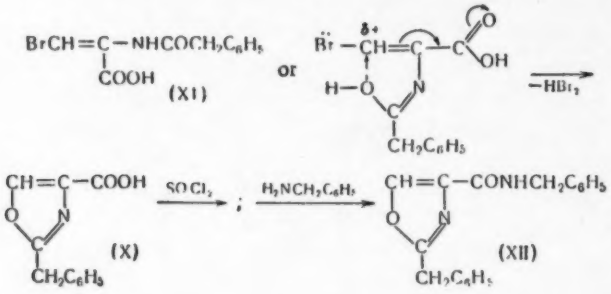
The substituents X in the α-position of α-acylamino-β-halocarboxylic acids can be arranged in the following order with respect to their effect on the rate of formation of acyloxypyruvic acids:



The ease with which HX is eliminated evidently depends on the electron density at the substituent, and the higher the electron density the more readily the reaction proceeds. This is best illustrated by using as examples compounds in which the substituent is an amino or an acylamino group; while the first is extremely unstable, the second is stable even on heating. However, if decomposition of the intermediately formed oxazoline (VIII) to the intermediate acid (IX) cannot occur, then elimination of the substituent X along with a hydrogen from the β-position becomes possible, and oxazolecarboxylic acids are formed.

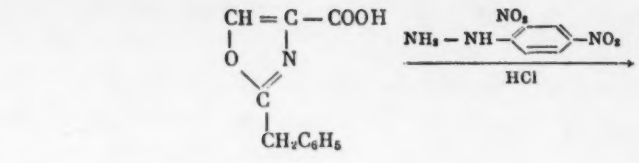


Indeed, under the prolonged action of an excess of 2 N NaOH or alcoholic NaOH, α-hydroxy-, α-methoxy-, and α-piperidino-α-phenylacetamido-β-halopropionic acids are readily converted in good yields to 2-benzyloxazole-4-carboxylic acid (X) (r is $CH_2C_6H_5$) with an m.p. of 153° (from water); this compound has previously been prepared by Conforth by another method [4]. A high yield of this same 2-benzyloxazole-4-carboxylic acid was obtained from β-bromo-α-phenylacetamidoacrylic acid (XI) or its ester. The action on (XI) of alcoholic solutions of bases or of sodium methylate in alcohol results in elimination of hydrogen halide with the formation of 2-benzyloxazole-4-carboxylic acid; this is a consequence of a nucleophilic attack by the hydroxyl oxygen of the lactim form of the amide on the highly electrophilic β-carbon atom of the conjugated acrylate system:

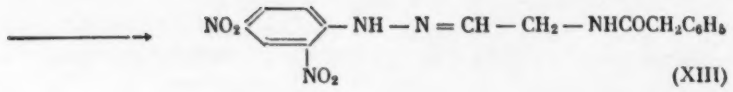


For proof of structure, (X) was converted by means of diazomethane to the methyl ester with an m.p. of 54°.

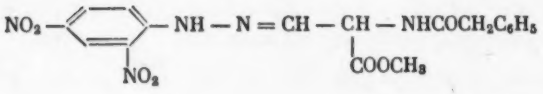
The action of thionyl chloride readily converted 2-benzyloxazole-4-carboxylic acid to the acid chloride; the latter was not isolated in the pure form, but it was converted by the action of benzylamine to 2-benzyloxazole-4-(N-benzyl)carboxamide (XII) with an m.p. of 119°. The literature gives an m.p. of 119-121° for this amide [5]. The action on (X) of a hydrochloric acid solution of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of 2-(phenylacetamido)acetaldehyde (XIII); in the case of 2-benzyl-4-carbomethoxyoxazole, this reaction gave the 2,4-dinitrophenylhydrazone (XIV) of the methyl ester of penaldic acid



(X)

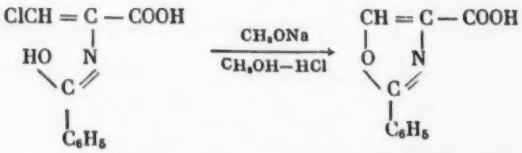


(XIII)



(XIV)

The action of a 1 N alcoholic solution of sodium methylate on β-chloro-α-benzamidoacrylic acid (XV) gave 2-phenyloxazole-4-carboxylic acid (XVI) with an m.p. of 208° (with decomposition). The melting point of 2-phenyloxazole-4-carboxylic acid prepared by a different method [6] was 209° (with decomposition).



(XV) (XVI)

EXPERIMENTAL

α-Ethylthio-α-benzamido-β-chloropropionic acid (II). 0.4 g of ethyl mercaptan was added to a solution of 1.3 g (0.005 mole of α,β-dichloro-α-benzamidopropionic acid in 100 ml of absolute ether, and the reaction mixture was allowed to stand at room temperature until the following day; the suspended matter was then filtered, the ether was evaporated at room temperature, and the residue was washed with water. 0.83 g of α-ethylthio-α-benzamido-β-chloropropionic acid, m.p. 113-114° (from alcohol by precipitation with water or ether), was obtained.

Found %: C 49.86; H 4.46. $C_{12}H_{14}O_3NS$. Calculated %: C 50.08; H 4.83.

α,β-Dibenzylthio-α-phenylacetamidopropionic acid (IV) (R = $CH_2C_6H_5$). 1.4 g of α,β-dibromo-α-phenylacetamidopropionic acid was mixed with 1 g of benzyl mercaptan, and the mixture stood at room temperature until the following day; it was then diluted with absolute ether and filtered. α,β-Dibenzylthio-α-phenylacetamidopropionic acid (hydrobromide), m.p. 135°, was obtained; the yield was 88%.

Found %: Br 13.8. $C_{25}H_{26}O_3NS_2Br$. Calculated %: Br 15.0.

When the reaction mixture was diluted with methanol instead of ether, a quantitative yield of α,β-dibenzylthio-α-phenylacetamidopropionic acid, m.p. 170-171° (from methanol), was obtained.

Found %: C 66.18; H 5.67; S 13.99; N 3.34. $C_{25}H_{25}S_2O_3N$. Calculated %: C 66.51; H 5.54; S 14.1; N 3.1.

α,β-Dibenzylthio-α-phenylacetamidopropionic acid was readily converted to β-benzylthio-α-phenylacetamidoacrylic acid, m.p. 178°, by the action of alcoholic NaOH on the compound in a 10% solution of $NaHCO_3$. A mixed sample with β-benzylthio-α-phenylacetamidoacrylic acid prepared by the action of benzyl mercaptan on β-bromo-α-phenylamidoacrylic acid showed no depression of the melting point. The reaction of

α,β-dibenzylthio-α-phenylacetamidopropionic acid with an ether solution of diazomethane gave the methyl ester with an m.p. of 70° (from ether).

Found %: C 66.79; H 5.71; S 13.51; N 3.47. $C_{26}H_{27}S_2NO_3$. Calculated %: C 67.09; H 5.8; S 13.76; N 3.0.

α,β-Dibenzylthio-α-benzamidopropionic acid (IV) (R=C_6H_5). To a solution of 1.3 g (0.005 mole) of α,β-dichloro-α-benzamidopropionic acid in 100 ml of absolute ether was added 0.6 g (0.005 mole) of benzyl mercaptan, and the mixture was allowed to stand at room temperature until the following day. On the following day, the precipitated α-benzamido-β-benzylthioacrylic acid was filtered, and the ether solution was promptly extracted in the cold with a solution of $NaHCO_3$ to a weakly alkaline reaction toward litmus and acidified with 2 N H_2SO_4. A mixture of α-benzamido-β-benzylthioacrylic acid and α,β-dibenzylthio-α-benzamidopropionic acid was precipitated, and the mixture was separated by fractional crystallization from ether. The following were obtained: 1) 0.3 g of α-benzamido-β-benzylacrylic acid with an m.p. of 207° (from a 50% solution of alcohol in ethyl acetate). A mixture with a known sample showed no depression of the melting point. 2) 0.6 g of α,β-dibenzylthio-α-benzamidopropionic acid with an m.p. of 131° (from ether).

Found %: C 65.88; H 5.30; S 16.85; N 3.35. $C_{24}H_{23}NS_2O_3$. Calculated %: C 65.90; H 5.26; S 16.93; N 3.2.

2-Benzyloxazole-4-carboxylic acid (X) (R=$CH_2C_6H_5$). a) 0.5 g of the methyl ester of α-piperidino-α-phenylacetylamido-β-bromopropionic acid was mixed with 5 ml of 2 N NaOH in methanol, and the mixture was allowed to stand at room temperature for 2 days. The alcohol was evaporated under vacuum at 20°. The residue was dissolved in 3 ml of water, extracted with ether, and the aqueous solution acidified with 2 N H_2SO_4. 0.25 g of 2-benzyloxazole-4-carboxylic acid, m. p. 152-153° (from water), was obtained; it crystallized with 1 molecule of water.

Found %: C 59.57; H 5.01; N 6.34. $C_{11}H_9O_3N \cdot H_2O$. Calculated %: C 59.70; H 4.97; N 6.33.

The melting point of 2-benzyloxazole-4-carboxylic acid purified by reprecipitation from ether with petroleum ether was 158-159°.

Found %: C 64.83; H 4.41. $C_{11}H_9O_3N$. Calculated %: C 65.02; H 4.43.

The melting point of 2-benzyloxazole-4-carboxylic acid prepared by a different method [4] was 158°. 2-Benzyloxazole-4-carboxylic acid was also prepared by the action of an excess of 2 N methanolic NaOH on α-methoxy-β-bromo-α-phenylacetamido and α,β-dibromo-α-phenylacetamidopropionic acids.

b) 0.3 g of the methyl ester of α-phenylacetamido-β-bromoacrylic acid was mixed with 1 ml of a 1 N solution of CH_3ONa in methanol (1 mole), the mixture was allowed to stand at room temperature for 3 days, and a solution of 2,4-dinitrophenylhydrazine was added. 0.4 g of the hydrazone, m.p. 148-151° (from absolute alcohol), was obtained. A mixture with a known sample isolated from natural penicilloic acid showed no depression of the melting point. Reaction of 2-benzyloxazole-4-carboxylic acid with an ether solution of diazomethane gave the methyl ester (XI) with an m.p. of 54° (from ether).

Found %: C 66.06; H 5.18; N 6.25. $C_{12}H_{11}O_3N$. Calculated %: C 66.34; H 5.07; N 6.45.

2-Benzyloxazole-4-carboxylic acid was treated with an excess of thionyl chloride; the mixture was evaporated under vacuum, and benzylamine was added to the residue. 2-Benzyloxazole-4-(N-benzyl)carboxamide, m.p. 117-118° (from absolute alcohol), was obtained.

Found %: C 73.72; H 5.59; N 9.68. $C_{18}H_{16}O_2N$. Calculated %: C 73.97; H 5.51; N 9.58.

When 2-benzyloxazole-4-carboxylic acid was heated for a brief time with a solution of 2,4-dinitrophenylhydrazine in 2 N HCl, the hydrazone of 2-(phenylacetamido)acetaldehyde (XIII) precipitated; m.p. 191-192° (from ethyl acetate). The literature gives an m.p. of 194-195° [7].

Found %: N 19.68. $C_{16}H_{14}O_5N_5$. Calculated %: N 19.4.

2-Phenyloxazole-4-carboxylic acid (XVI). 0.2 g (0.001 mole) of the methyl ester of α-benzamido-β-chloroacrylic acid was mixed with 2 ml of a 1 N solution of CH_3ONa in methanol; the mixture was allowed to stand for 48 hours at room temperature, evaporated under vacuum at 20°, dissolved in 2 ml of water, and acidified with 2 N H_2SO_4. 0.1 g of 2-phenyloxazole-4-carboxylic acid, m.p. 208° (from 30% alcohol), was obtained. The literature value is 208°.

SUMMARY

1. A new reaction for the formation of oxazolecarboxylic acids from α-diacylamido-β-haloacrylic acids was demonstrated.

2. α-Substituted α-acylamido-β-halopropionic acids were converted by the action of a base to oxazolinecarboxylic acids, which, depending on the conditions, readily formed either the acyloxypropionic acid or oxazolecarboxylic acids.

3. A mechanism was proposed for the formation of oxazolecarboxylic acids from α-acylamino-β-haloacrylic acids, and it was shown that the formation of oxazolecarboxylic acids from α-substituted α-acylamido-β-halopropionic acids proceeds, without preliminary transition to the corresponding α-acylamino-β-haloacrylic acids, through a stage in which 2-aryl-(or alkaryl)-4-substituted oxazoline-4-carboxylic acids are formed.

Institute of Heteroorganic Compounds
Academy of Sciences USSR

Received March 29, 1957

LITERATURE CITED

[1] O. V. Kil'disheva, M. G. Lin'kova, E. V. Benevolenskaia and I. L. Knuniants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 834.*

[2] O. V. Kil'disheva, M. G. Lin'kova and I. L. Knuniants, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 719.*

[3] O. V. Kil'disheva, M. G. Lin'kova and I. L. Knuniants, Bulll Acad. Sci. USSR, Div. Chem. Sci. 1955, 452.*

[4] The Chemistry of Penicillin, N. Y., 1949, p. 705.

[5] The Chemistry of Penicillin, N. Y., 1949, p. 707.

[6] The Chemistry of Penicillin, N. Y., 1949, p. 703.

[7] The Chemistry of Penicillin, N. Y., 1949, p. 825.

*Original Russian pagination. See C. B. Translation.

ACETYLENE DERIVATIVES

COMMUNICATION 191. PREPARATION OF ACIDS FROM TERTIARY ACETYLENIC ALCOHOLS

I. N. Nazarov, L. D. Bergel'son and V. I. Gunar

We have recently shown that cis-dibromovinylcarbinols (I) readily undergo dehydration and elimination of hydrogen bromide, forming thereby unstable 1-bromovinylacetylenes (III). The latter yield α,β- or β,γ-unsaturated acids when refluxed with a base [1].

$$(RCH_2)_2C(OH)-\overset{Br}{\overset{|}{C}}=\overset{Br}{\overset{|}{CH}} \rightarrow RCH=C(CH_2R)-\overset{Br}{\overset{|}{C}}=\overset{Br}{\overset{|}{CH}} \xrightarrow{KOH}$$

(I) (II)

$$\rightarrow RCH=C(CH_2R)-C\equiv CBr \xrightarrow[H_2O]{KOH} RCH=\underset{\displaystyle CH_2R}{\overset{\displaystyle |}{C}}-CH_2COOH \quad \text{or} \quad (RCH_2)_2C=CHCOOH$$

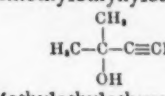
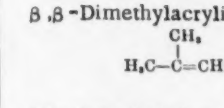
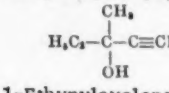
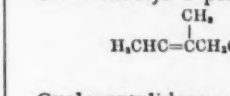
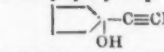
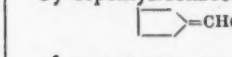
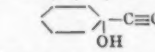
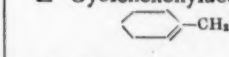
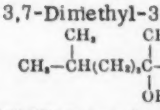
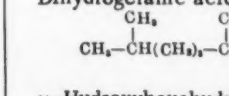
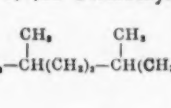
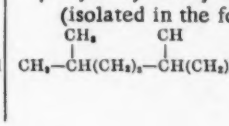
(III)

The present communication describes a method, based on the above reactions, for the preparation of unsaturated acids. With the aim of increasing the yield of substituted dibromobutadienes (II), we studied the dehydration of dibromovinylcarbinols (I) under the influence of heat and various dehydrating agents (potassium bisulfate, phosphorus pentoxide, p-toluenesulfonic acid, magnesium sulfate, sulfuric acid, and acetic anhydride). When water is eliminated from dibromocarbinols (I) in the absence of a catalyst (by distillation at 20-30 mm), the reaction does not usually go to completion [1]. Moreover, this method is not very suitable for the higher dibromovinylcarbinols, since the resulting dienic dibromides are high boiling and do not distill under the conditions of the reaction, and a lengthy time in the reaction medium leads to tar formation. Considerable tarring also accompanies the dehydration of cis-dibromovinyldimethylcarbinol under the influence of potassium bisulfate or magnesium sulfate. When cis-dibromovinylcyclohexanol is heated with sulfuric acid in acetic anhydride, a considerable amount of the acetate of the original alcohol is formed along with the dibromodiene.

The best results were obtained by refluxing the dibromovinylcarbinols in petroleum ether (b.p. 50-60°) with phosphorus pentoxide (in the case of cis-dibromovinyldimethylcarbinol) or p-toluenesulfonic acid (in the case of cis-dibromovinylcyclohexanol). Since bromination of the acetylenic alcohols is carried out in a petroleum ether medium, the dehydration can be carried out without isolating the brominated alcohols (I). The substituted dibromobutadienes (II) and, particularly, the vinylacetylenic bromides (III) are unstable, and they partially decompose and form tar during distillation. Therefore, it is expedient to carry out further operations, (dehydrobromination and alkaline hydrolysis,) in a single step without isolating the bromo derivatives (II) and (III). For this reason, the solution obtained after the dehydration is neutralized, the solvent is distilled, and the residue is refluxed for 30-40 hours with a solution of potassium hydroxide in aqueous methanol. In a number of cases, the conversion of acetylenic alcohols to unsaturated acids can be carried out under these conditions with satisfactory yields (Table 1).*

* After preparing the present paper for publication, we became acquainted with the article by Julia and Surzur [2], who obtained dimethylacrylic acid in 47% yield by the action of potassium hydroxide in methanol on the dihydropyranyl ether of dichlorovinyldimethylcarbinol.

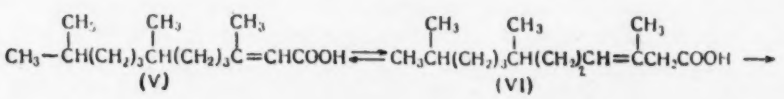
TABLE

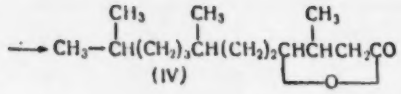
Expt. no.	Name and formula of original alcohol	Name and formula of acid	Yield in %	M.p. of S-benzyl-thiuronium salt in °C
1	Dimethylethynylcarbinol 	β,β-Dimethylacrylic acid 	55	152
2	Methylethylethynylcarbinol 	Cis-3-methyl-3-pentenoic acid 	34,5	121—122
3	1-Ethynylcyclopentanol 	Cyclopentylidenacetic acid 	24	142,5—143,5
4	1-Ethynylcyclohexanol 	Δ^1-Cyclohexenylacetic acid 	41,5	138—139
5	3,7-Dimethyl-3-octynol 	Dihydrogeranic acid 	66	123—124
6	3,7,11-Trimethyldodecynol 	γ-Hydroxyhexahydrofarnesenic acid (isolated in the form of the lactone) 	41	146—147,5

In those cases where the acids prepared are known, their constants are in satisfactory agreement with the literature values. In addition, all acids were characterized in the form of their S-benzylthiuronium salts, which have not previously been described in the literature. As may be seen from the Table, dimethylethynylcarbinol, 1-ethynylcyclopentanol, and 3,5-dimethyl-1-octyne-3-ol yield conjugated, α,β-unsaturated acids, while 1-ethynylcyclohexanol and methylethylethynylcarbinol are converted chiefly to β,γ-unsaturated acids. These results are in agreement with the data of Linstead and co-workers [3, 4], who found that cyclohexylideneacetic acid and 2-methyl-2-ethylacrylic acid are less stable than the corresponding Δ^1-cyclohexenylacetic acid and 3-methyl-3-pentenoic acid, and are converted to the latter when refluxed with a base.

Our S-benzylthiuronium salt of dihydrogeranic acid (m.p. 123-125°) differs from the preparation with an m.p. of 149° synthesized recently by Jocelyn and Polgar [5] by Reformatsky condensation of methylheptanone with bromoacetic ester. At the same time, the ultraviolet spectra of these two acids are identical and they indicate that the double bonds are conjugated. Finally, the structure of our dihydrogeranic acid was proved by ozonation to be 2-methyl-6-heptanone. Apparently, our acid and the acid of Jocelyn and Polgar are geometric isomers.

In the case of 3,7,11-trimethyl-1-dodecyn-3-ol, the chief product of the reaction was a lactone to which the structure of the lactone of γ-hydroxyhexahydrofarnesenic (4-hydroxy-3,7,11-trimethyldodecanoic) acid (IV) is assigned on the basis of its chemical properties and spectrum. Thus, the equilibrium between tetrahydrofarnesenic acid (V) and its β,γ-isomer (VI) in alkaline medium is obviously shifted toward the unconjugated acid (VI).

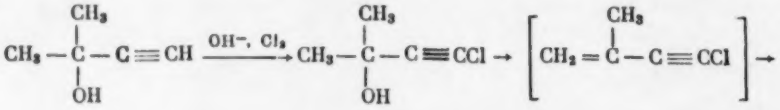


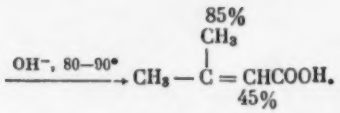


(IV)

Since we were unable to isolate γ-hydroxyhexahydrofarnesenic acid in the pure form owing to lactonization when the salt was acidified, the acid was characterized as the S-thiuronium salt.

γ,γ-Dimethylacrylic acid was also prepared from dimethylethynylcarbinol by a modification of the above-described method through dimethylchloroethynylcarbinol and 1-chloro-2-isopropylacetylene.





The two methods do not differ in number of steps; however, the bromination method gives somewhat higher yields.

EXPERIMENTAL

Preparation of β,β-dimethylacrylic acid: a) from dimethylethynylcarbinol. To a solution of 21 g of dimethylethynylcarbinol (b.p. 102-104°; n_D^{20} 1.4210) in 150 ml of petroleum ether (b.p. 50-60°) was added 41 g of bromine in 50 ml of petroleum ether; the reaction mixture was stirred and irradiated with a 200-w lamp during the addition, which was carried out at a rate such that the temperature of the reaction mixture did not exceed 35° (~1.5 hours). The stirring was then continued for an additional 30 minutes, after which the solution was washed with water, sodium hyposulfite solution, and again with water, and dried with magnesium sulfate. On the following day, the drying agent was filtered, and the filtrate was transferred to a three-neck flask; 40 g of phosphorus pentoxide was then added gradually while the reaction mixture was stirred and cooled with water. The mixture was then heated to boiling on a water bath, with vigorous stirring, and refluxing was continued for 1.5 hours. The organic layer was separated and washed with a saturated solution of sodium bicarbonate; about 150 ml of petroleum ether was then distilled under a slight vacuum. A solution of 90 g of potassium hydroxide in 300 ml of methanol was added to the residue, and the mixture was refluxed for 30 hours. A large part of the methanol was then distilled, 50 ml of water was added, and the neutral products were extracted with ether. The aqueous layer was carefully acidified with concentrated hydrochloric acid to precipitate crystals of β,β-dimethylacrylic acid, which were suction filtered. The filtrate was extracted with ether, and the extract was dried with magnesium sulfate; the ether was distilled, and the residue, which contained crystals, was distilled under vacuum. 14.5 g (56% yield) of β,β-dimethylacrylic acid, m.p. 69-70° (from water), was obtained. The amide of β,β-dimethylacrylic acid melted at 106-107° (from petroleum ether). The S-benzylthiuronium salt melted with decomposition at 152° (from 50% alcohol). According to the literature [6], β,β-dimethylacrylic acid has an m.p. of 70°, while the amide melts at 107-108°.

b) From dimethylchloroethynylcarbinol. A solution of 10.5 g of dimethylchloroethynylcarbinol [7] in 150 ml of petroleum ether was refluxed, with stirring, for 2 hours with 15 g of phosphorus pentoxide. The liquid layer was decanted from the sirup which had formed, and the petroleum ether was distilled under vacuum; a solution of sodium methylate (6 g of sodium in 150 ml of methanol) was added to the solution, and the mixture was refluxed for 30 hours. A solution of 10 g of potassium hydroxide in 50 ml of water was then added, and the refluxing was continued for 12 hours; the methanol was distilled the residue was extracted with ether, and the water layer was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was dried with sodium sulfate, the ether was distilled, and the residue was distilled under vacuum. 3.6 g (~45% yield) of β,β-dimethylacrylic acid was obtained; m.p. 69-70° (from water).

Preparation of cis-dibromovinylmethylethylcarbinol. To a solution of 60 g of methylethylethynylcarbinol (b.p. 118-122°; $n^{20}D$ 1.4226) in 100 ml of petroleum ether (b.p. 35-50°) was added 100 g of bromine in 100 ml of petroleum ether; the reaction mixture was stirred and irradiated with a 200-w lamp during the addition, which was carried out at a rate such that the temperature of the reaction mixture did not exceed 35-40° (3 hours). The stirring was continued for an additional 30 minutes. The mixture was washed with a sodium hyposulfite solution and then with water, dried with magnesium sulfate, and distilled under vacuum. A second distillation gave 106.5 g of cis-dibromovinylmethylethylcarbinol (77% yield); b.p. 68-69° (2.5 mm); $n^{20}D$ 1.5388; d^{20}_4 1.741; MR found, 46.61; MR calculated, 46.39.

Found %: C 27.94; 28.00; H 3.90; 3.86; Br 61.91; 61.69. $C_6H_{10}OBr_2$. Calculated %: C 27.93; H 3.95; Br 61.94.

Preparation of 3-methyl-3-pentenoic acid. a) From cis-dibromovinylmethylethylcarbinol. 60 g of cis-dibromovinylmethylethylcarbinol was added dropwise to 30 g of phosphorus pentoxide, which was contained in a Claisen flask connected to a condenser. An absolute pressure of 20 mm was maintained in the apparatus during the addition of the carbinol. An exothermic reaction began after several minutes, and the reaction was completed by heating the mixture under vacuum (8 mm) at a temperature of 80-90°. During the heating, 1,2-dibromo-3-methyl-1,3-pentadiene distilled at 55-59° (8 mm); $n^{25}D$ 1.5669; yield, 46.6 g (83%). The compound rapidly darkened on standing in air.

24 g of this diene was added to a solution of sodium methylate, which was prepared from 6 g of sodium and 350 ml of methanol. A precipitate of sodium bromide slowly formed. The mixture was refluxed for 20 hours; 75 ml of water was then added, and the refluxing was continued for an additional 10 hours. A large part of the methanol was distilled, the residue was extracted with ether, and the aqueous layer was acidified with concentrated hydrochloric acid (during which the mixture was cooled with ice water) and extracted with ether. The ether extract was dried with magnesium sulfate and distilled to yield cis-3-methyl-3-pentenoic acid, which contained, according to its refractive index, some 2-methyl-2-ethylacrylic acid; the yield was 8.8 g (77%); b.p. 98-102° (8 mm); $n^{20}D$ 1.4444; d^{20}_4 0.976. Three recrystallizations from petroleum ether, during which the solution was cooled with solid carbon dioxide in acetone, gave 6.3 g of pure cis-3-methyl-3-pentenoic acid with an m.p. of 1°.

The S-benzylthiuronium salt, after recrystallization from 50% alcohol, had an m.p. of 121-122°.

Found %: N 9.91; 9.98. $C_{14}H_{20}O_2N_2S$. Calculated %: N 10.0.

According to the literature [8], 3-methyl-3-pentenoic acid has a b.p. of 94-97° (7 mm); $n^{20}D$ 1.4430; d^{20}_4 0.9762.

b) From methylethylethynylcarbinol. Under the synthesis conditions used for the preparation of β,β-dimethylacrylic acid, 5.6 g of 3-methyl-3-pentenoic acid (34.5% yield) was obtained from 14 g of methylethylethynylcarbinol; b.p. 95-99° (7 mm); $n^{20}D$ 1.4451; the S-benzylthiuronium salt had an m.p. of 120-124°.

Preparation of cyclopentylideneacetic acid. a) To a solution of 12.5 g of 1-ethynylcyclopentanol in 150 ml of petroleum ether (b.p. 40-50°) was added a solution of 19 g of bromine in 100 ml of petroleum ether (the temperature of the reaction mixture was maintained at 35° by the heat of reaction and the irradiation); the reaction mixture was stirred and irradiated with a 200-w lamp during the addition. When the bromination was complete (after 2 hours), the mixture was washed with sodium hyposulfite solution and with water and dried with magnesium sulfate, and the solvent was distilled under vacuum. The residue was dissolved in 200 ml of benzene, 1.5 g of p-toluenesulfonic acid was added, and the mixture was refluxed, benzene and water distilling azeotropically. When the distillate had become transparent (after 2 hours and 30 minutes), the mixture was cooled, a solution of sodium methylate (10 g of sodium in 200 ml of methanol) was added, and the mixture was refluxed for 15 hours; 50 ml of water was then added, and the mixture was refluxed for another 10 hours. A large part of the methanol was then distilled, 50 ml of water was added to the residue, and the neutral products were extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether; the ether layer was dried with magnesium sulfate and distilled. 3.7 g (24% yield) of cyclopentylideneacetic acid, b.p. 130-140° (5 mm), was obtained; the product crystallized in the receiver. After a single recrystallization from 5% aqueous methanol, the acid had an m.p. of 50-52°. According to the literature [9], the m.p. is 51-52°.

The S-benzylthiuronium salt of cyclopentylideneacetic acid melted at 142° (from 60% alcohol).

Found %: N 9.57; 9.54. $C_{15}H_{20}O_2N_2S$. Calculated %: N 9.59.

From the ether extract of the alkaline solution was isolated ~11 g of undistillable, neutral, bromine-containing products with a sharp odor.

b) 0.7 g of cyclopentylideneacetic acid with an m.p. of 51-52° (from 5% aqueous methanol) was obtained from 12.5 g of 1-ethynylcyclopentanol under the conditions of the preceding experiment, except that the dehydration was carried out for 1 hour in boiling benzene (with azeotropic distillation of the water) in the presence of 3 g of magnesium sulfate.

Preparation of cyclohexenylacetic acid. 12.4 g of 1-ethynylcyclohexanol in 100 ml of petroleum ether (b.p. 50-60°) was brominated under irradiation as described above. The solution was washed with sodium hyposulfite solution and dried with magnesium sulfate; 1 g of p-toluenesulfonic acid was then added, and the mixture was refluxed for 2 hours. A large part of the petroleum ether was distilled under vacuum, and a solution of 16 g of potassium hydroxide in 150 ml of methanol was added to the solution. The mixture was refluxed for 30 hours, the methanol was distilled, 75 ml of water was added to the residue, and the mixture was extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid, and, on the following morning, 5.8 g of a mixture of cyclohexenylacetic and cyclohexylideneacetic acids (yields 42%), m.p. 30-36°, was filtered. Threefold recrystallization from 5% aqueous methanol gave 4.9 g of Δ^1-cyclohexenylacetic acid with an m.p. of 37-38°.

The S-benzylthiuronium salt melted at 138-139° (from 50% alcohol).

Found %: N 9.04; 8.99. $C_{16}H_{22}O_2N_2S$. Calculated %: N 9.12.

The literature [4] reports a melting point of 36-38° for cyclohexenylacetic acid.

The mother liquors were combined and evaporated to 10 ml. Storage of the residue in a refrigerator resulted in the precipitation of 0.57 g of cyclohexylideneacetic acid, which, after two-fold recrystallization from 5% aqueous methanol, melted at 89-91°.

The S-benzylthiuronium salt melted at 162-163° (from 50% alcohol).

Found %: N 9.59; 9.46. $C_{16}H_{22}O_2N_2S$. Calculated %: N 9.12.

4.6 g of a mixture of cyclohexenylacetic and cyclohexylideneacetic acids was obtained from 12.4 g of ethynylcyclohexanol under the above conditions, except that the dehydration was carried out in the presence of 15 g of phosphorus pentoxide in petroleum ether at 50-60° (the mixture was stirred for 1.5 hours).

Preparation of dihydrogeranic acid. 21 g of 3,7-dimethyl-1-octyne-3-ol, b.p. 70-73° (6 mm), $n^{20}D$ 1.4390 [10], and 0.3 g of benzoyl peroxide were dissolved in 200 ml of petroleum ether (b.p. 50-60°). A solution of 22.5 g of bromine in 100 ml of petroleum ether was added with vigorous stirring and at a rate such that the temperature of the reaction mixture did not exceed 35-40° (2 hours and 30 minutes). The mixture was washed with a saturated solution of sodium hyposulfite and with water and agitated for 15 minutes with anhydrous magnesium sulfate; 30 g of phosphorus pentoxide was added portion-wise, and the mixture was refluxed, with stirring, for 3 hours. 200 ml of water was added dropwise with cooling, the organic layer was evaporated under vacuum to a volume of 50 ml, and a solution of sodium methylate, prepared from 8 g of sodium and 250 ml of methanol was added. Sodium bromide slowly precipitated. The mixture was refluxed for 32 hours, and 100 ml of a 10% solution of sodium hydroxide in methanol was added; the mixture was refluxed for another 8 hours, and then a large part of the methyl alcohol was distilled. 250 ml of water was added to the residue, and the neutral products were extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether; the ether layer was dried with magnesium sulfate and distilled. 15.8 g (66% yield) of dihydrogeranic acid was obtained; b.p. 108-112° (2.5 mm); $n^{18}D$ 1.4542; d^{18}_4 0.931; MR found, 49.50; MR calculated, 49.45; λ_{max} 217 mμ; log ε 3.603* (in heptane).

Found %: C 70.39; 70.57; H 10.79; 10.71. $C_{10}H_{18}O_2$. Calculated %: C 70.54; H 10.64.

*The u. v. spectrum was taken by N. Zarakhan.

The S-benzylthiuronium salt of dihydrogeranic acid melted at 123-124° (from aqueous alcohol).

Found %: N 8.22; 8.47. $C_{18}H_{48}O_2N_2S$. Calculated %: N 8.33.

Ozonization of dihydrogeranic acid. Ozonized oxygen (6% ozone content) was passed for 6 hours through a solution of 4 g of dihydrogeranic acid in 40 ml of dry chloroform; 40 ml of 5% hydrogen peroxide was added, and the mixture was refluxed, with stirring, for 12 hours. The chloroform layer was separated, washed with sodium carbonate solution and with water, and dried with magnesium sulfate. The chloroform was distilled, and 2.6 g of 2-methyl-6-heptanone was obtained; b.p. 165-169°, $n^{20}D$ 1.4139. The semicarbazone of the ketone melted at 152-154° [11], and a mixture with a known sample showed no depression of the melting point.

Preparation of the lactone of γ-hydroxyhexahydrofarnesenic acid. Under irradiation from a quartz lamp, a solution of 11.5 g of bromine in 50 ml of petroleum ether was added to a solution of 15 g of 3,7,11-trimethyl-1-dodecyne-3-ol, b.p. 97-99° (1 mm), $n^{20}D$ 1.4487 [12], in 100 ml of petroleum ether (b.p. 50-60°); the addition was carried out at a rate such that the temperature of the mixture did not exceed 35° (~2 hours). The solution was washed with hyposulfite solution and dried with magnesium sulfate; 0.5 g of p-toluenesulfonic acid was then added, and the mixture was refluxed for 1 hour. After neutralization of the mixture with sodium carbonate, the solvent was distilled under vacuum, a solution of 50 g of potassium hydroxide in 200 ml of alcohol was added to the residue, and the mixture was refluxed for 40 hours. The alcohol was distilled, 100 ml of water was added, and the neutral products were extracted with ether. The aqueous layer was carefully acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was washed with water and dried with magnesium sulfate; the ether was distilled, and the residue was distilled under vacuum into two fractions, a neutral fraction with a boiling range of 103-108° (0.2 mm), $n^{18}D$ 1.4530, yield 6.6 g, and an acid fraction with a boiling range of 130-142° (0.2 mm), $n^{18}D$ 4632*, yield 2.0 g. A second distillation of the neutral fraction gave 6.2 g of the pure lactone of γ-hydroxyhexahydrofarnesenic acid with a b.p. of 87-88.5° (0.03 mm), $n^{18}D$ 1.4524; d^{18}_4 0.925. The infrared spectrum** had a band at 5.67μ (1758 cm^{-1}), which is characteristic of γ-lactones [13-15].

Found %: C 75.31; 75.38; H 11.85. $C_{15}H_{28}O_2$. Calculated %: C 74.93; H 11.74.

The acid fraction gave a mixture of S-benzylthiuronium salts which melted at 136-142° and which could not be resolved by crystallization from aqueous methanol.

0.5 g of the lactone of γ-hydroxyhexahydrofarnesenic acid was dissolved in 5% aqueous NaOH, and the solution was brought to a weakly alkaline reaction (toward phenolphthalein) with dilute hydrochloric acid. Upon the addition of S-benzylthiuronium chloride, the S-benzylthiuronium salt of γ-hydroxyhexahydrofarnesenic acid precipitated; m.p., 146-147.5° (from aqueous alcohol).

Found %: N 6.01; 6.07. $C_{26}H_{40}O_2N_2S$. Calculated %: N 6.31.

SUMMARY

A method was developed for the conversion of tertiary acetylenic alcohols to unsaturated acids.

N. D. Zelinskii Institute of
Organic Chemistry
Academy of Sciences USSR

Received March 27, 1957

LITERATURE CITED

[1] I. N. Nazarov and L. D. Bergel'son, J. Gen. Chem. (in press).***

[2] M. Julia and J. M. Surzur, Bull. Soc. chim. France 1956, 1620.

[3] G. A. R. Kon, R. P. Linstead and J. M. Wright, J. Chem. Soc. 1934, 602.

[4] R. P. Linstead, J. Chem. Soc. 1927, 355, 362.

[5] P. C. Jocelyn and N. Polgar, J. Chem. Soc. 1953, 132.

* As in original – Publishers note.

** The infrared spectrum was taken by B. B. Lopatnyi.

*** See C. B. Translation.

[6] F. De Laet, Bull. Soc. chim. Belg. 38, 163 (1929); Chem. Abstrs. 23, 4443 (1929).

[7] F. Straus, L. Kollek and W. Heyn., Ber. 63, 1868 (1930).

[8] R. B. Wagner, J. Amer. Chem. Soc. 71, 3214 (1946).

[9] G. A. Kon and R. P. Linstead, J. Chem. Soc. 127, 621 (1925).

[10] J. R. Naves and P. Ardizio, Helv. chim. acta 31, 1240 (1948).

[11] O. Wallach, Ann. chimie 408, 185 (1915); P. Karrer and K. S. Jap, Helv. chim. acta 23, 581 (1940).

[12] F. G. Fischer and K. Lõwenberg, Ann. chimie 475, 183 (1929).

[13] R. Rasmussen and R. R. Brattain, J. Amer. Chem. Soc. 71, 1073 (1949).

[14] G. S. Skinner and R. de V. Huber, J. Amer. Chem. Soc. 73, 3321 (1951).

[15] E. E. Van Tamelen and M. Shamma, J. Amer. Chem. Soc. 76, 2315 (1954).

TRANSFORMATIONS OF MOLECULES IN AN AQUEOUS MEDIUM

Krishna Bahadur and S. Ranganayaki

From time immemorial, savants and scholars the world over have attempted to penetrate the veil of mystery surrounding the origin of life on earth. The recently held International Symposium on the Origin of Life on Earth [1] developed the views of the various scholars on this question; these views may possibly be reduced to the idea that life, or protoplasm, was formed as a result of the slow transformation of matter found on the surface of the earth.

The simplest organic and inorganic substances combined and formed amino acids, which, by further condensation, formed peptides and proteins. Adenylic acid and nucleic acids were formed independently of one another, and the combination of proteins, nucleic acids, and adenylic acid acquired the ability to divide. This system possessed the property of generating its own energy. Gradually, this system evolved into primitive protoplasm. The primitive protoplasm was sensitive to changes in the surrounding environment, and the changes stimulated by the environment were reproduced in the duplicates resulting from division. The physical forces promoting the formation of biochemically important compounds have been studied. Thus, Miller [2] reported that if an electric discharge is passed through a mixture of methane, hydrogen, ammonia, and water vapor, certain amino acids are synthesized. Investigation of the effect of light on the formation of amino acids has shown that if a sterilized mixture of paraformaldehyde, potassium nitrate, and water is subjected to the action of light in the presence of ferric chloride as a catalyst, several amino acids are synthesized [3]. The formation of these amino acids is certainly connected with the formation of free radicals. The following reaction mechanism has been proposed for their formation [4]:

$$CH_2O + OH_2 \rightleftarrows CH_3OH + HCOOH$$
$$CH_2O + HCOOH \rightleftarrows OHCH_2COOH \ .$$
$$OHCH_2COOH \rightleftarrows CHOCOOH + 2H$$
$$CHOCOOH + NH_3 \rightleftarrows NH : CHCOOH + OH_2$$
$$NH : CHCOOH + 2H \rightleftarrows NH_2CH_2COOH \text{ (glycine)}$$
$$NH : CHCOOH + CH_2O \rightleftarrows CHOCH(NH_2)COOH$$
$$CHOCH(NH_2)COOH + 2H \rightleftarrows OHCH_2CH(NH_2)COOH \text{ (serine)}$$

The concentration of hydrogen ions in the irradiated solution exerts an enormous effect on the nature of the amino acids synthesized, and the amino acids synthesized in the mixture undergo photolysis; the changes they undergo depend on the exposure time [5]. A similar mechanism for the photosynthesis of natural amino acids was described in our previous article [6]. The formation of alanine and glycine, simultaneously with the formation of small amounts of valine, histidine, glutamic acid, and ornithine, occurs when a sterlized mixture of paraformaldehyde, water, and colloidal molybdenum oxide is subjected to irradiation by the light from a 500-W lamp [7]. This interesting observation was confirmed by Professor L. Santamaria of Milan University. In this synthesis of amino acids in a mixture free from fixed nitrogen, the nitrogen of the amino acids is fixed from the atmosphere. Carbon compounds undergo oxidation under the influence of light, and the free radicals formed in the mixture combine with the nitrogen of the amino acids. It has been observed and reported that the fixation of nitrogen during irradiation of an aqueous solution of carbon dioxide proceeds in the presence of colloidal molybdenum

oxide as a catalyst [8]. A mixture of 400 ml of doubly distilled water and 20 ml of colloidal molybdenum oxide were placed in a 500 ml conical flask; the mixture was sterilized at a pressure of 1.0546 kg/sq. cm. (15 psig) for 30 minutes, and then was maintained at a temperature of 30° for 24 hours, after which it was again sterilized as just described. A similar mixture was prepared and held in the dark. After sterilization, the flasks were placed in a closed compartment in an atmosphere of carbon dioxide for 24 hours. One of the flasks was covered with a heavy, dark material, and then both of these flasks were exposed to light of a 500-w lamp every day for 1 month. Alanine and glycine were formed in the mixture in the uncovered flask, while no amino acids were detected in the mixture in the flask which was protected from the light. In this experiment, the carbon dioxide in the mixture, on exposure to irradiation, formed organic compounds, which, on further exposure, revealed the development of free radicals capable of combining with atmospheric nitrogen. The experiments on the photosynthesis of amino acids showed that the formation of amino acids proceeds in an aqueous mixture containing carbon compounds or dissolved carbon dioxide plus the nitrogen required for the formation of amino acids; this nitrogen is not necessarily only combined nitrogen present in the mixture, but may also be atmospheric nitrogen. The amino acids synthesized in this manner can be acted upon by bacteria, but when there was no life on the earth, these compounds remained on the surface of the earth for long periods of time and further combination of them was possible. The energy required for the formation of peptide bonds is the same as that required for the formation of dipeptides and is shown in Table 1.

TABLE 1

Free Energy Required for the Formation of Peptide Bonds

Reacting substance	Reaction product besides water	ΔF°_{298}, cal.
Alanine-glycine	Alanylglycine	3730
Glycine-glycine	Glycylglycine	3230
Leucine-glycine	Leucylglycine	2960

Thus, approximately 3 to 4 thousand calories is required for the formation of a peptide bond. Considering the requirement that the acquisition of energy is necessary for the formation of peptide bonds, Fox [10] investigated the thermal route for the synthesis of peptides. He reported that the formation of certain peptides by heating amino acids in the temperature range of 180 to 200° is possible. This was a discovery of a simpler process for the synthesis. It was noted that a series of peptides is synthesized when a mixture of amino acids, water, and, for example, carbohydrates is placed in the sunlight [11]. A 0.1% solution of glycine and a 2% solution of sucrose were prepared, and 100 ml of each solution was transferred to each of two 250 ml Sigcol flasks and also to a single 250 ml quartz flask. These flasks were sterilized. One of the Sigcol flasks was covered with a heavy, black material, and all three solutions were placed in the sunlight for 7 hours daily over a period of 30 days. The solutions in the flasks were analyzed chromatographically and by the biuret method for peptide content. The peptides found in the solutions are reported in Table 2.

In this peptide synthesis, the energy required for the formation of the peptide bonds came partly from irradiation with photons. The energy of the ultraviolet region of the spectrum, which penetrated only into the quartz vessel, promoted the synthesis of the peptide bonds.

The formation of peptide bonds in aqueous solutions of glycine was also observed by Gurvich in his own experiments on the autosynthesis of "enzymoids." He reported that in the presence of an appropriate matrix, "enzymoids" are synthesized from enzymes after irradiation of a dilute solution of glycine [12]. The "enzymoids" have peptide bonds, and the formation of these peptides proceeded as a consequence of irradiation. Thus, it becomes clear that even under the physicochemical conditions presently existing on earth, photosynthesis of amino acids and peptides can occur. This synthesis, if it does occur, can easily lead to the formation of peptide complexes of high molecular weight and also of proteins. This could be one of the processes by which amino acids and proteins were created during that period before life appeared on earth.

The amino acid–peptide mixture was synthesized in the presence of adenylic acid, nucleic acids, and various other carbon compounds by photosynthesis from simple materials or from decomposition products or products of ensuing reactions of previously synthesized compounds; this mixture together with various inorganic compounds formed a mixture which acted as the substrate for an endless variety of reactions yielding compounds of vastly higher and differing molecular weights. However, of the numerous series of compounds thus formed, there remain only those compounds which were stable under the physicochemical conditions of the earth in the periods in which they were formed; they survived and led to succeeding reactions.

TABLE 2

Photosynthesis of Peptides in Glycine Solution in the Presence of Sucrose

Vessel	Peptides found
Sigcol flask protected from light	–
Sigcol flask not protected from light	Glycylalanine
Quartz	Glycylalanine, glycylnorleucine, glycylglycine

Life, as we understand it, now has the ability to multiply; it has its own system for the release of energy and the ability to adjust to the surrounding environment. Of these properties, multiplication has been the center of attention for some time past. The role of irradiation in the multiplication process has been investigated through the autosynthesis of enzymoids. It has been found that in experiments in which a solution of glycine was irradiated with mitogenetic radiation [13] in the presence of a matrix of enzyme, enzymoids were synthesized. The composition spectrum of the latter agrees with the spectrum of compounds formed as a result of enzymatic reactions of enzymes. These experiments showed that if a mixture contains the ingredients required for the formation of a molecular structure possessing the same mitogenetic spectrum as a structure formed by multiplication of the matrix, and if this mixture is then activated by the required amount of radiation, a duplicate of the matrix is formed. It has been shown experimentally that, in spite of the fact that enzymoids have the same chemical activity as the matrix enzyme, they differ chemically from the enzymes causing their formation. In spite of the possible existence of certain molecular structures with the same mitogenetic composition, there will be synthesized only that structure of formation of which is the more probable considering the components of the irradiated mixture and the physicochemical conditions existing in the zone of multiplication. This explains the existence of only a small number of isomers among naturally occurring organic compounds, for which a great many isomers are possible. For example, of the possible 512 possible steroid isomers [14], we find only isomers of cholestane and coprostane existing in nature. Similarly, of the series of amino acids, only a few of them exist as natural amino acids.

It has been pointed out that certain protein molecules react with mitogenetic radiation and become radiants [15]. Radiation induced in this manner possesses the following important properties: the secondary radiation originates from the irradiated part of proceeds through the liquid medium for a distance of several centimeters and at a measurable rate of several meters per second; the radiation is resonant, i.e., the substrate reacts chiefly at the same wavelengths that they imitate during enzymatic decomposition.

Irradiation of a mixture as described above converts it to a dynamic mixture in which the numerous compounds of differing molecular structures will continuously change into other structures possessing almost the same level of energy. If two similar structures A and B are synthesized in this mixture and if these structures react so that A remains unchanged while B decomposes into different molecules, then this system will act as a substrate–enzyme complex, and will imitate the wave length λ [15, 16]. This radiation causes the formation in the mixture of those compounds which can imitate λ. Thus, compounds of different molecular structures are synthesized; the most stable of these remain, while the unstable ones decompose. These compounds act more effectively in combination with adenylic acid, since the system releases its own energy, and is not very dependent on an external source of radiation. The external physicochemical changes act on the structure of these molecular systems; strong changes decompose them, while insignificant changes produce only small changes in the molecular structure. These changes are transmitted to the succeeding derivative structures, of which only the stable structures adapted to chemical transformations of the molecules are preserved. It was in this manner that a system was formed which was capable of contraction, which had a system for the release of energy, and which possessed the property of adjusting to the medium; it was the primoidal protoplasm which gradually developed to the present form of life. This mechanism of the emergence of life not only indicates that the physicochemical conditions which brought about the emergence of life on earth still exist on the earth at the present time, but it also shows that reactions which led to the emergence of life occur at the present time. Moreover, this demonstrates that even on other planets with different physicochemical conditions, systems are formed which are in equilibrium with the physicochemical conditions of the planet and which are capable of multiplication. These systems will have their own system for the release of energy, will react with the surrounding medium, and will be capable of adjusting to small physicochemical changes and then gradually transform into a higher form of life.

SUMMARY

1. Experiments were carried out on the photosynthesis of amino acids in an aqueous medium from carbon dioxide and atmospheric nitrogen in the presence of molybdenum oxide; experiments were also carried out on the photosynthesis of the simplest peptides from an aqueous solution of glycine and sugar.

2. A hypothesis was proposed for the photosynthesis of amino acids, peptides, and albumins and for their further evolution.

Department of Chemistry
Allahabad University
India

Received April 8, 1958

LITERATURE CITED

[1] International Symposium on the Origin of Life on Earth, held in Moscow in August, 1957.

[2] L. Miller, Ann. N. Y. Acad. Sci. 69, 2, 260-275 (1957).

[3] K. Bahadur, Nature 173, 1441 (1954).

[4] K. Bahadur and S. Ranganayaki, Compt. rend. 240, 246 (1955).

[5] K. Bahadur and S. Ranganayaki, Proc. Natl. Acad. Sci., India 23, A. I, 21-24 (1954).

[6] Collected reports of the international symposium, Izd. Acad. Sci. USSR, 1957, p. 90.*

[7] K. Bahadur, S. Ranganayaki and L. Santamaria, Report International Symposium on Origin of Life on the Earth (1957).

[8] K. Bahadur and S. Ranganayaki, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 754.**

[9] H. M. Huffman, J. Phys. Chem. 46, 885 (1942).

[10] S. W. Fox, et al., Ann. N. Y. Acad. Sci. 69, 2, 328 (1957).

[11] K. Bahadur and S. Ranganayaki, Paper communicated for the symposium on Biochemical Origins held at San Francisco, USA in April (1958).

[12] A. Gurvich, Enzymologia 12, 20, 11, 139 (1947).

[13] O. Rahn, Invisible Radiations of Organisms, Protoplasma Monographien, 9, Verlag Von Gebruder Borntraeger, Berlin, 1936.

[14] H. Gilman, Organic Chemistry, 2nd ed., John Wiley and Sons, Inc. London, 1944, p. 1367.

[15] A. Gurvich, I Internat. Congress of Electro-Radio Biology, Venice, 1934.

[16] A. M. Karpass and M. N. Lanschina, Biochem.-Z. 215, 337 (1929).

*In Russian.

**Original Russian pagination. See C. B. Translation.

SYNTHESIS AND PROPERTIES OF α-CYANOISOPROPOXYSILANES AND α-CYANOISOPROPOXYCHLOROSILANES

COMMUNICATION 2

A. D. Petrov and V. M. Vdovin

The synthesis of organosilicon compounds with α-cyanopropoxy groups on the Si atom was first carried out by Frisch and Wolf [1] and independently by Hahn [2]. The first two of these authors also found that $(CH_3)_3SiOC(CH_3)_2CN$ is hydrolyzed with difficulty, apparently because of the branched nature of the radical. In a previous communication [3] we have shown that the synthesis of such compounds with several α-cyanoisopropoxy groups on the silicon proceeds readily and with good yields even in the case of $[NCC(CH_3)O]_4Si$, while the synthesis of $[tert\text{-}C_4H_9O]_4Si$ requires severe reaction conditions [4]. In the present investigation we have studied: 1) the influence of the structure of the alkyl-(aryl)-chlorosilanes on the yield of their mono-, di- and tri-α-cyanoisopropoxy derivatives under conditions where there is an insufficient amount of acetonecyanohydrin at room temperature; 2) the behavior of the various cyanoisopropoxysilanes toward hydrolyzing agents in the presence and absence of pyridine; 3) the behavior of dialkyl-α-cyanoisopropoxychlorosilanes toward a Grignard reagent.

It follows from the data given in Table 1 that the alkyl-(aryl)-halosilanes investigated can be divided into three groups. In the first group belong CH_3SiHCl_2 and $C_2H_5SiHCl_2$, which give only completely substituted derivatives. This property obviously is not general for the alkyldichlorosilanes, since already in the case of $n\text{-}C_3H_7SiHCl_2$ we were able to isolate $(n\text{-}C_3H_7)ClHSi[OC(CH_3)_2CN]$; apparently here the effect of the known steric hindrance of the n-propyl radical is indicated. It is curious that the property of CH_3SiHCl_2 of giving completely substituted derivatives is characteristic of this compound even under less favorable conditions; thus, when the ratio of the chloride to acetonecyanohydrin was increased to 4:1, the dilution with benzene was greater, and the temperature was −10°, even then we isolated only the disubstituted derivative. In the second group belong the alkyl- and dialkyldichlorosilanes No. 3-6 (Table 1), which give mono- and disubstituted derivatives. Finally, as can be seen from Table 1, the presence of the phenyl radical on the silicon atom leads to the formation only of monosubstituted products.

A study of the hydrolysis revealed a distinct difference in the behavior of the alkyl-(aryl)-α-cyanoisopropoxysilanes and that of the dialkyl-α-cyanopropoxychlorosilanes. The former are rather stable toward hydrolysis (see No. 1-11 in Table 2), and even $CH_3Si[OC(CH_3)_2CN]_3$, which has three ether groups, is unchanged in contact with water and when kept in a moist atmosphere with a considerable amount of HCl. Compounds of the second type – $R_2SiCl[OC(CH_3)_2CN]$, where R = CH_3 or C_2H_5, are hydrolyzed practically instantaneously by water, both at the $\equiv Si—Cl$ bond and at the $\equiv Si—O$ bond, according to the equation

$$R_2[NC(CH_3)_2CO]SiCl + 2H_2O \rightarrow HCl + HOC(CH_3)_2CN + R_2Si(OH)_2 \rightarrow [R_2SiO]_n + H_2O.$$

We were able to find conditions under which hydrolysis took place only at the Si—Cl bond, namely an insufficient amount of water in a benzene solution of pyridine

$$2R_2SiCl[OC(CH_3)_2CN] + 2C_5H_5N + 2H_2O \rightarrow 2HCl \cdot C_5H_5N +$$
$$+ 2R_2Si(OH)[OC(CH_3)_2CN] \rightarrow R_2[NCC(CH_3)_2O]SiOSi[OC(CH_3)_2CN]R_2.$$

TABLE 1

Effect of Radicals Attached to Silicon on the Substituting Capacity of Acetonecyanohydrin

No.	Forumla of silicochloride used in reaction with acetonecyanohydrin	Ratio of chloride to alcohol in moles	Yield in %	
			mono-substituted product	disubstituted product
1	CH_3SiHCl_2	3 : 1	0	64
2	$C_2H_5SiHCl_2$	3 : 1	0	50,5
3	$(CH_3)_2SiCl_2$	3 : 1	56,2	30
4	$(C_2H_5)_2SiCl_2$	3 : 1	68,3	15,3
5	$C_2H_5SiCl_3$	3 : 1	55,6	11,8
6	$(ClH_2C)CH_3SiCl_2$	5 : 2	44,0	39,4
7	$C_6H_5SiCl_3$	3 : 1	82,2	0
8	p-$ClC_6H_4SiCl_3$	2 : 1	93,9	0

TABLE 2

Behavior Toward Hydrolysis of Alkyl- and Aryl-α-cyanoisopropoxysilanes

No.	Formula of compound	Contact time in hours	Degree of hydrolysis in %	Reaction conditions: stirring compound with excess hydrolyzing agent at 20 ± 2°
1*	$(CH_3)_3SiOC(CH_3)_2CN$	8	0	H_2O
2*	Ditto	8	60	5% HCl
3*	" "	16	45	5% NaOH
4	$(C_2H_5)_2Si[OC(CH_3)_2CN]_2$	8	0	H_2O
5	$(CH_3)C_6H_5Si[OC(CH_3)_2CN]_2$	18	0	H_2O
6	$(CH_3)Si[OC(CH_3)_2CN]_3$	8	0	H_2O
7	Ditto	8	74,5	5% HCl
8	" "	300	0	Kept in air with high content of HCl and moisture (50%)
9	$(C_6H_5)Si[OC(CH_3)_2CN]_3$	300	0	Under conditions of expt. No. 8 in sat. benzene soln.
10	Ditto	9 months	0	Under conditions of expt. No. 8
11	$(CH_3)_2ClSiOC(CH_3)_2CN$	0,2	100	H_2O
12	Ditto	0,2	> 80	With 1 g-equiv. of H_2O at –15°
13	$(C_2H_5)_2Si[OC(CH_3)_2CN]Cl$	0,2	100	

*Experiments 1-3 were carried out by Frisch [1]. It is interesting that under the conditions of experiment 1 $(CH_3)_3Si(OC_2H_5)$ is more than 60% hydrolyzed.

$R_2Si[OC(CH_3)_2CN]_2$ was obtained as a by-product in these syntheses, most probably from a reaction between the starting monochloride and the acetonecyanohydrin produced by partial hydrolysis of this monochloride at the $\rangle Si-OC(CH_3)_2CN$- group.

The $[(C_2H_5)_2SiOC(CH_3)_2CN]_2$ prepared by us proved to be identical with the by-product obtained in the synthesis of $(C_2H_5)_2Si[OC(CH_3)_2CN]_2$ [3]. Thus it is apparent that in the case of this synthesis a side reaction took place with the formation of disiloxane. This same reaction may explain the formation of higher boiling fractions also in the synthesis of other compounds of the type $RR'Si[OC(CH_3)_2CN]_2$.

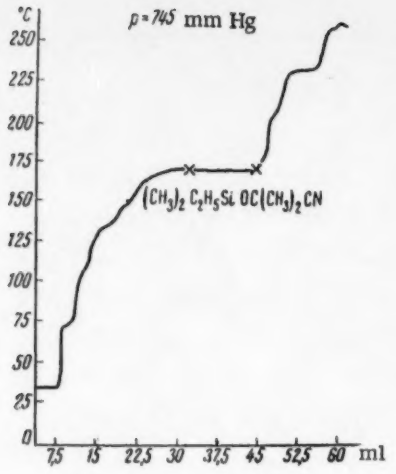


Fig. 1.

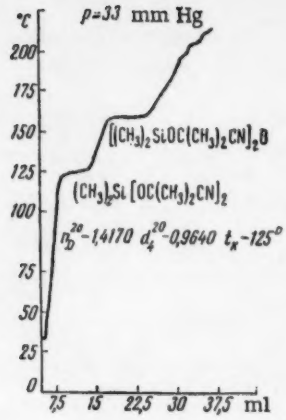


Fig. 2.

We were able, under similar conditions of hydrolysis at a temperature of −10 to −15°, to observe the formation of silicones from a new sort of dichlorosilanes – the alkyl-α-cyanoisopropoxydichlorosilanes – according to the reaction:

$$(C_2H_5)Cl_2SiOC(CH_3)_2CN + 2H_2O + 2C_5H_5N \rightarrow 2[HCl \cdot C_5H_5N] +$$
$$+ (C_2H_5)[NCC(CH_3)_2O]Si(OH)_2 \rightarrow [(C_2H_5)[NCC(CH_3)_2O]SiO]_n.$$

The formation of the silicones was quantitative. The higher fraction separated by distillation at 0.5 mm apparently consisted of cyclic polysiloxanes.

We also attempted to prepare trialkyl-α-cyanoisopropoxysilanes, which are very stable to hydrolysis, by the reaction:

$$ClR_2SiOC(CH_3)_2CN + R'MgX \rightarrow R_2R'SiOC(CH_3)_2CN.$$

However, the Grignard reagent reacted not only at the $\geq Si-Cl$ bond, but also at the $\geq Si-O$ and $-C\equiv N$, as a result of which we were only able to obtain compound No. 2 (Table 3) from $(CH_3)_2ClSi[OC(CH_3)_2CN]$ and $BrMgC_2H_5$ in small yield from a mixture of many materials (Fig. 1). In the case of this same chloride and other Grignard reagents, C_6H_5MgBr, n-C_4H_9MgBr, and n-C_4H_9MgI, we were not able to isolate individual products. We also did not succeed in preparing trialkylcyanoisopropoxysilanes from the dichlorides and Grignard reagents.

Thus, the most acceptable method of preparing the trialkyl-α-cyanoisopropoxychlorosilanes will be by synthesis from trialkylchlorosilanes, obtained by the Grignard synthesis, and acetonecyanohydrin (No. 15, Table 3).

EXPERIMENTAL

I. Synthesis of alkyl-(aryl)-α-cyanoisopropoxysilanes and alkyl-(aryl)-α-cyanoisopropoxychlorosilanes. The synthesis, the results of which are given in Table 3, was carried out by a method described by us previously [1]. In all experiments a benzene solution of acetonecyanohydrin was added at the rate of 0.3-0.4 mole per hour to a solution of silicochloride (1 g-equivalent in 450-500 ml of benzene). In the syntheses of No. 8, 9, 12, and 15 we used equivalent amounts of the reagents; after the reagents were mixed, the reaction mixture was heated for 2-3 hours at the boiling point of the benzene. In the synthesis of No. 6 the compound corresponding to the formula $(CH_3)C_3H_7Si[OC(CH_3)_2CN]_2$ was not obtained, but disiloxane No. 7 was isolated. In the synthesis of No. 14 a considerable amount of higher boiling material was noted, but we were not able to isolate individual products from it. In the synthesis of No. 13 the molar ratio of $C_6H_5SiCl_3$ to acetonecyanohydrin was 1:2. For the rest of the syntheses the ratio of silicochloride to alcohol is shown in Table 1; in Table 3 the compounds prepared for the first time are described.

TABLE 3

No.	Formula of compound	Yield in %	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.
1	$(CH_3)_2ClSi-O-C(CH_3)_2CN$	56,2	82 (25)	1,4166	1,0052	44,41	44,32
2	$(CH_3)_2C_2H_5SiOC(CH_3)_2CN$	28,4	169,5 (746)	1,4110	0,8641	49,25	49,22
3	$H(C_2H_5)Si[OC(CH_3)_2CN]_2$	64	92,5—93 (3)	1,4210	0,9653	59,25	59,28
4	$(C_2H_5)_2ClSiOC(CH_3)_2CN$	68,3	76 (6)	1,4296	0,9922	53,51	53,60
5	$(ClH_2C)(CH_3)ClSiOC(CH_3)_2CN$	44	83—4 (6)	1,4429	1,1452	49,15	49,18
6	$(C_3H_7)(CH_3)ClSiOC(CH_3)_2CN$	45,7	91,5 (15)	1,4263	0,9828	53,60	53,60
7	$[CH_3(C_3H_7)SiOC(CH_3)CN]_2O$	4,2	156—158 (5)	1,4300	0,9867	95,30	96,27
8	$CH_3CHClSi[OC(CH_3)_2CN]_3$	56,5	170 (5)	1,4393	1,0882	83,19	82,92
9	$C_6H_5Si[OC(CH_3)_2CN]_3$	41,7	191 (2)	Crystals 62,5—3°			
10	$p\text{-}ClC_6H_4Si[OC(CH_3)_2CN]Cl_2$	93,9	124 (2)	1,5139	1,2763	69,38	68,65
11	$[(CH_3)_2SiOC(CH_3)_2CN]_2O$	27	159,5 (33)	1,4150	0,9696	77,96	77,78
12	$CH_3Si[OC(CH_3)_2CN]_3$	61,5	126 (1)	1,4219	1,0155	73,90	73,57
13	$C_6H_5SiCl[OC(CH_3)_2CN]_2$	41,5	162 (3)	1,4817	1,1110	79,20	78,59
14	$Cl(C_3H_7)HSi[OC(CH_3)_2CN]$	30	82—83 (13)	1,4219	0,9886	49,26	49,23
15	$(CH_3)_2(H\text{-}C_4H_9)SiOC(CH_3)_2CN$	70,5	102—2,5 (20)	1,4195	0,8552	58,93	58,60

II. Hydrolysis in the absence of pyridine. The hydrolysis conditions are given in Table 2. The reaction products were extracted with ether or benzene, dried with $CuSO_4$, and distilled. The yield of unchanged product and the presence of acetonecyanohydrin showed the degree of hydrolysis. It should be noted that slight contamination with chlorides of the type $R_mClSi[OC(CH_3)_2CN]_n$, where m + n = 3, leads to complete hydrolysis of the compound under the conditions of No. 1-10 (Table 2).

III. Preparation of symmetrical tetraalkyl-bis-(α-cyanoisopropoxy)disiloxanes. In a flask with a stirrer were placed 21.4 g of $(C_2H_5)_2ClSiOC(CH_3)_2CN$, and 9.6 g of pyridine in 150 ml of benzene. 0.88 g of H_2O was added to the contents at the rate of a drop per minute. After a half-hour's stirring the precipitate was filtered by suction and the benzene solution was distilled. Upon distillation of the residue in vacuo, the compound was isolated in 43% yield; b.p. 152-154° (4.5 mm); $n^{20}D$ 1.4342; d^{20}_4 0.9710; MR found 95.61; MR calculated for $[(C_2H_5)_2SiOC(CH_3)_2CN]_2O$ 95.42.

We had previously obtained this compound as a by-product [3] with the constants $n^{20}D$ 1.4332; d^{20}_4 0.9734; MR found 95.23. $[(CH_3)_2SiOC(CH_3)_2CN]_2O$ was prepared in a similar manner. When the compound was distilled on a 20-plate column, we obtained a second fraction (Fig. 2) as well as the main reaction product No. 11 (Table 3); this compound had properties very close to those of $(CH_3)_2Si[OC(CH_3)_2CN]_2$ prepared by Frisch [1], b.p. 124-6° (21 mm); $n^{20}D$ 1.4174; d^{20}_4 0.9644.

IV. Preparation of ethyl(α-cyanoisopropoxy)polysiloxane. Ethyl(α-cyanoisopropoxy)polysiloxane was prepared by a method similar to that described previously from 53 g of $(C_2H_5)Cl_2SiOC(CH_3)_2CN$, 39.5 g of C_5H_5N, and 4.5 g of H_2O at a temperature of −15°. After addition of the water had been completed, stirring was continued for another 5 hours. After this time the temperature slowly rose to that of the room and a precipitate separated out; the latter was filtered by suction and washed with benzene; it weighed 26.5 g, which indicated the reaction had gone to completion. After the starting materials had been distilled off, the viscous, odorless oil was distilled under reduced pressure:

Found %					Calculated %				
C	H	Si	Cl	N	C	H	Si	Cl	N
				7,87					7,85
56,11	10,15	15,72			56,08	9,98	16,37		
56,16	10,09	15,48							
52,40	7,96	12,62		12,05	53,05	8,01	12,39		12,38
52,16	8,13	12,20		12,08				None	
46,66	7,91	13,60	14,97	6,57	46,71	7,78	13,63	14,20	6,83
47,71	7,91	13,75	14,84						
34,08	5,10	13,11			33,96	5,22	13,22		
32,49	5,31	13,26							
46,87	7,79	13,32			46,71	7,78	13,63		
47,20	7,89	13,74							
52,70	8,94	15,30			53,92	9,04	15,73		
	8,92								
48,78	6,39	7,45	10,48		48,89	6,44	8,16	10,31	
48,72	6,61	7,58	10,38						
60,63	6,78	7,88			60,48	6,49	7,89		
60,61	6,61	8,24							
41,38	3,70	9,52			4,79	3,42	9,52		
41,23	3,62	9,36							
47,46	8,35	18,14			47,83	8,05	18,67		
	8,34	18,42							
52,01	7,09	8,81			52,85	7,16	9,48		
52,99	7,22	9,57							
				9,36					9,07
				9,14					
44,07	7,57	14,24			43,94	7,36	14,63		
44,27	7,78	14,48							
59,90	10,75	14,79			60,2	10,6	14,1		
59,95	10,78	14,41							

Fract. I, b.p. 170-200° (0.5 mm); found N 9.54; 9.34%.

Fract. II, b.p. 240-280° (0.5 mm); found N 9.13; 9.05%; Si 17.76; 17.90%.

Residue, viscous oil N 6.35; 6.26%.

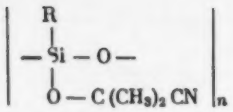
Calculated for $(C_2H_5)(NCC(CH_3)_2O)SiO$ N 8.92; Si 17.83%.

V. Reaction with RMgX. The Grignard reagent prepared from 17.3 g of C_2H_5Br in 100 ml of ethyl ether over a period of 3.5 hours was added to a solution of 44.5 g of $(CH_3)_2ClSiOC(CH_3)_2CN$ in 150 ml of ether, after which stirring was continued for 3 hours; after standing for a day the content of the flask was decomposed with water, the water layer was extracted, etc. The ether solution was dried over Na_2SO_4, the ether was distilled off, and the residue was distilled on a column. Compound No. 2 (Table 3) was isolated from the complex mixture of reaction products. When we attempted to use n-C_4H_9MgBr and C_4H_9MgI in the reaction with the above-named chloride, the mixture was more complex and even when we employed effective vacuum columns we were not able to isolate individual compounds.

SUMMARY

1. The synthesis of 13 different α-cyanoisopropoxysilanes has been accomplished for the first time. It has been shown that the nature of the radicals linked with the silicon, when there is a deficiency of acetonecyanohydrin, determines the number of α-cyanoisopropoxy groups that go onto the silicon.

2. Conditions have been found for the preparation of a new type of polysiloxanes



and considerable stability toward hydrolysis has been demonstrated in compounds of the type $R_mSi[OC(CH_3)_2CN]_n$, where n = 1, 2, 3 and m + n = 4.

LITERATURE CITED

[1] K. C. Frisch and W. Wolf, J. Organ. Chem. 18, 657 (1953).

[2] W. Hahn, Makromolek. Chem. No. 1, 64 (1953).

[3] A. D. Petrov, V. F. Mironov and V. M. Vdovin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 1122.*

[4] H. Breederveld and H. I. Waterman, Research 6, 485 (1953).

N. D. Zelinskii Institute of
Organic Chemistry of the
Academy of Sciences USSR

Received March 27, 1957

*Original Russian pagination. See C. B. Translation.

REACTION OF TRIMETHYLSILYLMETHYLMAGNESIUM CHLORIDE WITH ESTERS

E. V. Kukharskaya, D. N. Andreev and V. A. Kolesova

Trimethylhalomethylsilanes [$(CH_3)_3SiCH_2X$] are the simplest halosilanes capable of forming Grignard complexes. These complexes react normally with ethylene oxide [1], propylene oxide [2], acetaldehyde [3], benzaldehyde [4], acetone [4], acetic anhydride [4], and CO_2 [5], forming the corresponding oxygen-containing organosilicon compounds: primary, secondary, and tertiary alcohols, ketones, and acids. Recently Petrov, Ponomarenko, and Snegova have published the results of an investigation [6] in which they showed the $(CH_3)_3SiCH_2MgCl$ reacts normally also with ethyl formate, and in this instance the tertiary alcohol formed undergoes dehydration and β-decomposition as a result of the rupture of one of the Si—C bonds.

In the present work we have investigated the reaction of trimethylsilylmethylmagnesium chloride with ethyl esters of acetic, and n- and isobutyric acids. It has been established that with the first two esters the reaction proceeds normally in the direction of the formation of tertiary alcohols, but is also accompanied by β-decomposition, the splitting out from the tertiary alcohol of one $(CH_3)_3Si$- radical as a result of breaking of the Si—C bond. This fact was not unexpected, since it had already been noted in the publications of a number of investigators that organosilicon β-alcohols [3, 6], like β-acids [3, 5], ketones [4], and esters [7], easily undergo rupture of the Si—C bonds under the influence of electrophilic and nucleophilic agents.

$$2\,(CH_3)_3SiCH_2MgCl + RCOOC_2H_5 \rightarrow (CH_3)_3SiCH_2-\underset{\displaystyle R}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_2Si(CH_3)_3$$

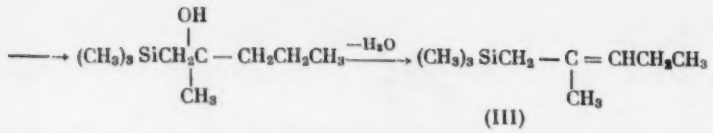
$$\downarrow H^+$$

$$(CH_3)_3SiCH_2\underset{\displaystyle R}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_3 + (CH_3)_3SiOH$$

In our experiments we did not succeed in isolating in pure form the tertiary organosilicon alcohols formed as a result of β-decomposition. In an experiment with ethyl acetate we isolated 2-(trimethylsilylmethyl)propene (I) [$(CH_3)_3SiCH_2(CH_3)C{=}CH_2$], the constants of which proved to be identical with those of trimethylmethyllylsilane previously obtained by Petrov and Nikishin [8] in another way. The Raman spectrum of (I) also was very similar to the data for the compound reported in reference [8], with the exception of several weak lines and divergences in the region 165-190 cm^{-1}.

In an experiment with ethyl n-butyrate we obtained an unsaturated silicohydrocarbon with the composition $C_9H_{20}Si$ (II). To confirm its composition we carried out the counter synthesis, starting with methyl propyl ketene:

$$(CH_3)_3SiCH_2MgCl + CH_3COCH_2CH_2CH_3 \longrightarrow$$



(III)

In this experiment also we were unable to isolate the tertiary alcohol. We obtained an unsaturated silicohydrocarbon with the same composition $C_9H_{20}Si$ (III), the constants of which were very close to those of (II). However, the Raman spectra of (II) and (III) differed noticeably, indicating that their structures were different. Examination of the spectra of compounds (II) and (III) showed that in both cases the frequencies 1630 and 3080 cm^{-1}, which are characteristic of the vibration of the C=C bond in the β-position, were present, and the frequencies 1594-1623 and 3050 cm^{-1}, which are typical of vinylsilanes, were absent. Thus, in both compounds there was a double bond in the β-position.

From data in the literature it is known that the shift of a double bond from the end position to the middle of the chain usually causes an increase in the vibration frequency of the C=C bond of 20-30 cm^{-1}. In the substituted vinylsilanes, in which the double bond is in the middle of the chain, the vibration frequency of the C=C bond is increased to 1621-1623 cm^{-1} compared with 1594 cm^{-1} for the unsubstituted vinylsilanes [9]. In a similar way, the vibration frequency of the C=C bond in the β-position changes, depending on whether it is in the end position (1630 cm^{-1}) or in the middle of the chain (1651 cm^{-1}) [10]. The intense frequency 1661 cm^{-1} that occurs in the spectrum of (III) must be ascribed to the C=C bond that is in the β-position in the middle of the chain. The somewhat increased value of the frequency for this bond (increased by 10 cm^{-1}) can be explained by the presence of a side methyl group linked with one of the carbon atoms of the double bond. The effect of side methyl groups at the double bond on the increases in the frequency of the C=C bond has been noted previously in one of the publications cited [9]. In the spectrum of compound (II), on the other hand, the frequency 3080 cm^{-1} is present (antisymmetric frequency of C–H in the $=CH_2$ group) and the frequency 1661 cm^{-1} is absent, indicating the end location of the double bond in the β-position to the silicon atom.

Thus, from the spectroscopic data it follows that (II) and (III) are isomers, to which the following structures can be ascribed:

(II) (III)

2-(Trimethylsilylmethyl)pentene-1 2-(Trimethylsilylmethyl)pentene-2

The presence in the spectrum of (III) of the lines 1634 cm^{-1} (5) and 3089 cm^{-1} (1/2) which are very weak in comparison with the spectrum of (II) permits the assumption that there was a small admixture of (II) in compound (III). The absence from the spectra of all three of the silicohydrocarbons of the frequencies characteristic of compounds that contain a double bond in the α-position to the silicon atom indicates that dehydration of the tertiary alcohols prepared by us takes place as a result of splitting off of hydrogen atoms only from the carbon atoms that are in the γ-position to the silicon; i.e., in a manner similar to that observed by Petrov, Ponomarenko, and Snegova [6].

In the experiment with the ethyl ester of isobutyric acid we were not able to isolate the tertiary alcohol or olefin. We recovered 73% of unreacted ethyl isobutyrate and a small amount of reaction products that boiled over a wide temperature range. The branched structure of the acid apparently produced considerable steric hindrance that hampered the course of the reaction.

Comparison of the results of the experiments with methyl propyl ketone and with the esters permits the conclusion that organosilicon β-alcohols containing one $(CH_3)_3Si$- radical in the molecule are rather stable and do not undergo β-decomposition as a result of the action of dilute mineral acids to a noticeable degree. The presence in the organosilicon β-alcohol molecules of two such radicals renders the alcohols very unstable, so that they undergo β-decomposition readily under the influence of dilute mineral acids with the formation of tertiary alcohols containing but one silicon atom.

EXPERIMENTAL

Reaction of trimethylsilylmethylmagnesium chloride with ethyl acetate. From 48.6 g (2 moles) of magnesium, 245.5 g (2 moles) of $(CH_3)_3SiCH_2Cl$, and 600 ml of dry ether we prepared the Grignard reagent, to which we added 83.7 g (0.95 mole) of ethyl acetate. The mixture was then heated with stirring for 16 hours, the ether was distilled off, and the complex was heated in an oil bath for 24 hours at 110-120°. Then the ether that had been distilled off was added to the flask, the complex was decomposed with dilute hydrochloric acid, the ether layer was separated, washed with sodium carbonate solution and with water, and dried with anhydrous $CuSO_4$. After the ether had been distilled off, the residue was fractionated. We obtained 17.7 g (0.2 mole) of the starting ethyl acetate, 16 g of hexamethyldisiloxane (b.p. 99-101°), and 14.5 g (15% yield) of 2-(trimethylsilylmethyl)-propene (I); b.p. 110.5-111°; $n^{20}D$ 1.4191; d^{20}_4 0.7395; found MR 43.70; calculated MR 43.82. Literature data [8]: b.p. 111-111.5°, $n^{20}D$ 1.4193; d^{20}_4 0.7397.

Raman spectrum* of (I) $\Delta\nu$ cm^{-1}: 191 (8 w. d.), 233(8), 261(1), 387(1 d), 423(2), 488(6), 535 (1), 594(12), 654(1), 691(3), 772(1 d), 829(2 d), 868(2 d), 1065(0), 1119(3), 1160(5), 1247(1), 1278(1), 1397(4), 1411(6), 1441(0), 1635(10), 2896(12), 2914(4), 2960(12), 2980(3), 3076(2).

Reaction of trimethylsilylmethylmagnesium chloride with ethyl n-butyrate. From 36.5 g (1.5 moles) of magnesium, 183.9 g (1.5 moles) of $(CH_3)_3SiCH_2Cl$, and 500 ml of dry ether we prepared the Grignard reagent, to which we added 77 g (0.66 mole) of ethyl n-butyrate. The mixture was heated with stirring for 12 hours and after cooling it was decomposed with dilute hydrochloric acid. The ether layer was separated, washed with sodium carbonate solution and water, and dried with anhydrous $CuSO_4$. After the ether had been distilled off, the residue was fractionated. We obtained 17.3 g (17% yield) of 2-(trimethylsilylmethyl)pentene-1 (II); b.p. 152-153° (757 mm); d^{20}_4 0.7675; $n^{20}D$ 1.4282; found MR 52.41, calculated MR 52.96.

Found %: C 68.73; 68.78; H 13.21; 13.14; Si 17.92; 18.10. $C_9H_{20}Si$. Calculated %: C 69.14; H 12.89; Si 17.96.

$\Delta\nu$ cm^{-1}: 171(2 d), 199(5 d), 238(7), 265(1), 354(1 d), 408(1 d), 435(1 d), 462(1 d), 533(5), 193(10), 616(7), 658(1), 693(7), 714(1), 750(1), 772(1), 838(3 d), 872(3 d), 907(1 d), 1040(3), 1126(5), 1159(6), 1219(1 d), 1285(2 d), 1301(2 d), 1395(3), 1418(4), 1452(3), 1633(15), 2879(5), 2908(15), 2962(15), 2984(2), 3080(3).

By fractional distillation in vacuo we obtained 12.6 g of material with b.p. 86-87.5° (7 mm); $n^{20}D$ 1.4452; d^{20}_4 0.8504; found MR 54.98; calculated MR 54.58, which from the analytical data and constants apparently was the tertiary alcohol of the composition $(CH_3)_3SiCH_2C(OH)(CH_3)CH_2CH_2CH_3$ [printed as $(CH_3)_3SiCHC(OH)CH_2CH_2CH_3$ with CH_3 below], containing a little impurity. When heated, this compound decomposes and formed a number of compounds, among them (I).

Reaction of trimethylsilylmethylmagnesium chloride with methyl propyl ketone. From 167 g (1.36 moles) of $(CH_3)_3SiCH_2Cl$, 33.0 g (1.36 moles) of magnesium, and 400 ml of ether we prepared the Grignard reagent, to which we added 77.5 g (0.9 mole) of methyl propyl ketone. The ether was distilled off and the complex was heated in an oil bath at 110-125° for 12 hours. Then the ether that had been distilled off was added to the flask and the complex was decomposed with dilute hydrochloric acid. The ether layer was separated, washed with sodium carbonate solution and water, and dried with anhydrous $CuSO_4$. After the ether was distilled off, we obtained 30.2 g (0.35 mole) of the starting methyl propyl ketone and 30 g (32% yield) of 2-(trimethylsilylmethyl)-pentene-2 (III): b.p. 153-154°: $n^{20}D$ 1.4290; d^{20}_4 0.7670; found MR 52.54; calculated MR 52.96.

Found %: C 69.04; 69.19; H 13.00; 12.90; Si 17.91; 18.00. $C_9H_{20}Si$. Calculated %: C 69.14; H 12.89; Si 17.96.

$\Delta\nu$ cm^{-1}: 182(5), 196(7), 236(8), 268(1), 364(0), 435(0), 601(12), 617(1), 693(10), 751(1), 762(1), 869(4), 911(3), 1031(2), 1145(1), 1159(8), 1205(6), 1256(7), 1300(7), 1356(1), 1375(1), 1413(8), 1453(8), 1634(5), 1661(12), 2886(3), 2960(1), 2909(15), 2972(15), 3089(½).

---

* The Raman spectra were obtained on an ISP-51 spectrograph. Excitation was effected from the 4358 A mercury line. The violet portion of the radiation was filtered with a saturated aqueous solution of $NaNO_2$. The intensity of the lines was evaluated visually.

SUMMARY

1. The reaction between trimethylsilylmethylmagnesium chloride and the ethyl esters of acetic and n-butyric acids proceeds normally, in the direction of the formation of tertiary alcohols, but is accompanied by β-decomposition, the splitting off from these alcohols in acid medium of one trimethylsilyl group.

2. When tertiary organosilicon alcohols containing a hydroxyl group on the β-carbon atom are dehydrated, unsaturated silicohydrocarbons are formed with a double bond in the β-position.

LITERATURE CITED

[1] L. Sommer, R. Van Strien and F. Whitmore, J. Amer. Chem. Soc. 71, 3056 (1949).

[2] S. Brynolf, Acta Chem. Scand. 10, 1143 (1956).

[3] F. Whitmore, L. Sommer, J. Gold and R. Van Strien, J. Amer. Chem. Soc. 69, 1551 (1947).

[4] C. Hauser and C. Hance, J. Amer. Chem. Soc. 74, 5091 (1952).

[5] L. Sommer, J. Gold, G. Goldberg and N. Marans, J. Amer. Chem. Soc. 71, 1509 (1949).

[6] A. D. Petrov, V. A. Ponomarenko and A. D. Snegova, Proc. Acad. Sci. USSR 112, 79 (1957).*

[7] J. Gold, L. Sommer and F. Whitmore, J. Amer. Chem. Soc. 70, 2874 (1948).

[8] A. D. Petrov and G. I. Nikishin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 243.*

[9] A. D. Petrov, Iu. P. Egorov, V. F. Mironov, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 50.*

[10] A. D. Petrov, G. I. Nikishin, N. P. Smetankina, and Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 947.*

Institute of Silicate Chemistry
of the Academy of Sciences USSR

Received March 20, 1957

*Original Russian pagination. See C. B. Translation.

ISOLATION OF HIGHER n-ALKANES FROM THE 190-350° FRACTION OF SOKOLOVOGORSK AND MIRZAAN PETROLEUMS

N. G. Bekauri, N. I. Shuikin, Iu. P. Egorov and T. S. Shakarashvili

In recent years, in connection with progress in the area of building motors that operate on medium and heavy petroleum distillates, there has arisen a need for preparing these products with good motor qualities. At present it is very essential to investigate the chemical nature of these distillates and to explore ways of improving their motor properties. One of the most widely used methods for the investigation of the individual composition of the paraffin portion of the kerosene–gasoline fraction of a petroleum is the formation of complexes of the normal alkanes with urea. This method has been used in a number of investigations by Soviet and foreign workers who have devoted their attention to the determination of the individual composition of the higher alkanes. Thus, for example, Rozenberg and Genekh [1] investigated the conditions for complex formation by urea and the normal alkanes from various petroleums of the Soviet Union. Nekrasova and Shuikin [2, 3] identified n-undecane and n-dodecane in fractions of Crimean petroleum. Nikolaeva, Zvereva, Zimina, and Popova [4] separated individual hydrocarbons with a composition from $C_{12}H_{26}$ to $C_{20}H_{42}$ from Romashkin petroleum by the use of urea. Interesting studies in this field were carried out by Schlenk, Jr. [5], Damazk and Kobe [6], Hepp, Box, and Ray [7], and Swern [8], who in their investigations solved the problem of the investigation of the nature of the complexes and the separation of the individual hydrocarbons from mixtures, and also of the preparation of reactive fuels by the treatment of kerosene fractions with urea.

The objective of the present work was the separation of the alkanes from the kerosene–gasoline fraction with b.p. 190-350° obtained from direct distillation of Sokolovogorsk and Mirzaan petroleums. Using the methods and procedures described in previous publications [1-6], we separated in sufficiently pure form and identified the alkanes of normal structure that enter into the make-up of the kerosene–gasoline fraction with b.p. 190-350°, with compositions from $C_{11}H_{24}$ to $C_{20}H_{42}$ inclusive. At the present time we are engaged in studying the conditions for their contact-catalytic isomerization.

EXPERIMENTAL

As subjects for the present investigation we selected kerosene–gasoline fractions of petroleums from the Sokolovogorsk (Ural) and Mirzaan (Georgia) deposits. By direct distillation of the petroleum samples under laboratory conditions we separated fractions boiling within the limits 190-350°. The properties of the distillates obtained from the Sokolovogorsk and Mirzaan petroleums are given in Table 1.

After the properties of the two samples had been determined, a gradual and successive simplification of the hydrocarbons entering to their composition was carried out. For this purpose we first removed the aromatic hydrocarbons by chromatographic adsorption. As the adsorbent we used activated silica gel of the ASM Voskresenskii Chemical Combine make. The characteristics of the mixtures of aromatic hydrocarbons that were separated and of the refined products are presented in Table 2. The refined materials obtained were treated with 10% sodium hydroxide solution in order to remove a part of several sulfur and oxygen compounds. Then from each sample of refined product of the dearomatized kerosene–gasoline fraction we separated by complexing with urea the normal alkanes, which had the following properties. From Sokolovogorsk petroleum: b.p. 185-346° (730 mm); $n^{20}D$ 1.4455; d^{20}_4 0.8239; aniline point 84.9°. From Mirzaan petroleum: b.p. 182-342° (745 mm); $n^{20}D$ 1.4380; d^{20}_4 0.7540; aniline point 90.0°.

TABLE 1

Properties of Fraction with b.p. 190-350° from Sokolovogorsk and Mirzaan Petroleums

Origin of fraction with b.p. 190-350°	n_D^{20}	d_4^{20}	Aniline point in °C	Setting point in °C	Sulfur content in %	Heating capacity in cal/kg (highest)
Sokolovogorsk	1,4660	0,8229	69,2	—20	0,019	10 855
Mirzaan	1,4717	0,8448	63,9	—25	0,099	10 754

TABLE 2

Properties of Refined Products and Aromatic Hydrocarbons Separated from Samples of Fraction with b.p. 190-350°

Starting samples of fraction with b.p. 190-350°	Mixture of aromatic hydrocarbons			Refined product			
	b.p. in °C at 20 mm	n_D^{20}	d_4^{20}	b.p. in °C at 18 mm	n_D^{20}	d_4^{20}	aniline point in °C
From petroleum of Sokolovogorsk deposit	86—230	1,5323	0,9512	75—224	1,4467	0,8066	85,3
From petroleum of Mirzaan deposit	89—228	1,5425	0,9659	73—221	1,4419	0,8510	82,6

TABLE 3

Comparison of Group Composition of Samples of Fraction with b.p. 190-350° Determined by Different Methods (in wt. %)

Fraction with b.p. 190-350°	Aniline method				Separation of n-alkanes with urea (direct method)			
	Aromat. hydrocarbons	Cyclanes	n- and isoalkanes	Aniline pt. of mixture of cyclanes and alkanes (°C)	Aromat. hydrocarbons	n-Alkanes	Mixture of cyclanes and isoalkanes	Aniline pt. of mixt. of cyclanes and isoalkanes (°C)
From petrol. of the Sokolovogorsk deposit	22,9	39,3	37,8	82,5	22,9	34,7	42,2	81,7
From petrol. of the Mirzaan deposit	28,0	45,4	26,6	80,1	28,0	8,5	64,2	78,9

The mixtures of isoalkanes and cyclanes that remained after removal of the n-alkanes were characterized by the following properties. From the fraction of Sokolovogorsk petroleum with b.p. 190-350°: b.p. 174-325° (742 mm); $n^{20}D$ 1.4530; d^{20}_4 0.8307; aniline point 81.7°. From the fraction of Mirzaan petroleum with b.p. 190-350°: b.p. 178-330° (742 mm); $n^{20}D$ 1.4552; d^{20}_4 0.8396; aniline point 78.9°.

Thus, by the use of adsorption–displacement chromatography and extractive crystallization with urea it proved possible to establish the group composition of the fractions taken for investigation. The results obtained are compared in Table 3 with the group composition data determined by the aniline method [9].

TABLE 4

Physicochemical Properties of Hydrocarbons Separated

No.	Normal alkanes	Properties of hydrocarbons separated							Literature data [12]		
		b.p. in °C at 736 mm	d_4^{20}	n_D^{20}	setting point in °C	aniline point in °C	*MR* calculated	*MR* found	b.p. in °C at 760 mm	d_4^{20}	n_D^{20}
1	Undecane	193,5	0,7413	1,4182	—26	80,3	52,99	52,13	195,8	0,7402	1,4172
2	Dodecane	212—213	0,7488	1,4220	—11,5	84	57,62	57,80	216,275	0,7488	1,4216
3	Tridecane	229—230	0,7577	1,4259	—6,5	87,1	62,23	62,27	235,5	0,7562	1,4255
4	Tetradecane	243—244	0,7636	1,4292	+5	89,8	66,85	66,97	253,6	0,7626	1,4291
5	Pentadecane	265—266	0,7681	1,4320	7,7	91,9	71,47	71,72	270,6	0,7683	1,4319
6	Hexadecane	282—283	0,7735 *	1,4346	15,5	94,4	76,98	76,32	287,1	0,7734	1,4345
7	Heptadecane	302—304	0,7819	1,4360 30°	26	99,6	85,32	85,75	317,5	0,7823	1,4350 30°
8	Octadecane	289—290	0,7786	1,4370	19	97,6	80,70	80,97	302,7	0,7779	1,4368
9	Nonadecane	321—323	0,7862	1,4336 40°	31,5	101,6	89,94	90,25	331,7	0,7774 at m.p.	1,4330 40°
10	Eicosane	334—337	0,7883	1,4348 40°	35	103,7	94,56	94,94	345,3	0,7889 20°	1,4345 40°

* Specific gravities were determined at melting points and calculated by the formula $d^{20}_4 = d^t_4 + \gamma(20 - t)$ [15].

Separation of the mixture of normal alkanes from the dearomatized fraction was carried out by mixing a definite amount of urea with the material under investigation in the presence of methanol. It was established that the longer the hydrocarbon chain, the greater was the stability of the complexes toward temperature. We found that in a series of alkanes with composition $C_{11}-C_{20}$ the ratio of the weight of urea to the volume of normal alkane used was almost constant. On the average it was equal to 2.52 g of urea per ml of n-alkane in the presence of 15% absolute methanol as activator. The mixture was carefully stirred for 2-3 hours on a mechanical shaker. The suspension of crystals that was formed was filtered with the aid of a water pump, the crystals were washed 3 times with isopentane and then dried at room temperature between sheets of filter paper. After this they were dissolved in water heated to 60°. The oily layer of normal alkanes was separated in a separatory funnel, dried with calcium chloride, and then distilled.

The mixture of normal alkanes obtained in the amount of 10 liters (6.9 liters was obtained from 20.2 liters of the fraction with b.p. 190-350° from Sokolovogorsk petroleum, and 3.1 liters from 35.3 liters of the Mirzaan fraction) was fractionated from a special type of Claisen flask with a large dephlegmator at a pressure of 1 mm Hg into fractions that were collected within the limits of the boiling points of the normal alkanes of composition $C_{11}-C_{20}$. At first comparatively broad fractions were obtained, which boiled within the following ranges:*

184-205°, 6.8% C_{11} (consisted mainly of C_{11}); 205-210°, 0.6% (C_{11}-C_{12});** 210-220°, 9.2% (C_{12});

220—229° — 2,0% (C_{12}—C_{13});	229—240° — 10% (C_{13});
240—260° — 9,8% (C_{14});	260—264° — 0,8% (C_{14}—C_{15});
264—270° — 10,2% (C_{15});	270—281° — 2,5% (C_{15}—C_{16});
281—292° — 9,8% (C_{16});	292—296° — 0,5% (C_{16}—C_{17});
296—307° — 10% (C_{17});	307—312° — 0,7% (C_{17}—C_{18});
312—323° — 7,0% (C_{18});	323—329° — 0,8% (C_{18}—C_{19});
329—340° — 8,6% (C_{19});	340—348° — 8,2% (C_{20}); residue 2,4%.

The fractions obtained were then redistilled over sodium into narrower fractions within boiling ranges of not more than 2-3° on a vacuum fractionating column with an efficiency of 75 theoretical plates at a pressure of 1-2 mm. The individual nature of the hydrocarbons separated was established by determination of the boiling and setting points, the specific gravity, and the index of refraction. For final purification from possible contaminants, the hydrocarbons of composition $C_{11}H_{24}-C_{17}H_{36}$ that were obtained were passed through 300 g of silica gel that was placed in a column heated with hot water (60-70°) and maintained at constant pressure by means of a gasometer.

Since the hydrocarbons of composition $C_{18}H_{38}-C_{20}H_{42}$ were solids at room temperature, they were identified by fractional crystallization; i.e., by systematic and successive separation of small fractions of the crystals of the individual compounds. All the hydrocarbons separated except n-nonadecane and eicosane boiled within limits of 1-2°. In the course of the work, the hydrocarbons of composition $C_{17}-C_{20}$ were treated with 2% oleum or antimony pentachloride by Shaarschmidt's method [11] to purify them of isoalkanes. As can be seen from the data of Table 4, the hydrocarbons obtained had properties very close to those indicated in the literature [12].

To verify the purity of the n-alkanes obtained, we turned to the infrared absorption spectra. In one recent publication [13] a method had been indicated for determining the degree of branching of isoalkanes of composition $C_{12}-C_{16}$, and this method had already been used for the analysis of decanes [14]. According to the observations of Egorov, the number of CH_2 groups can be determined from the IR band at 3.42 μ, which by virtue of the low intensity of the 3.38 μ band (characteristic of the CH_3 group) appears almost independent. The IR spectra of the alkanes of composition $C_{11}-C_{20}$ obtained by this method were similar in the region 3-4 μ, with gradually rising magnitude of the peak at 3.42 μ and a decrease in the total length of the absorption peak at 3.38 μ. As an example, the spectral curves for the extreme members of the series, n-undecane and n-eicosane, are shown in Fig. 1 in the 3-4 μ region (transmission in % on the ordinate axis).

*The boiling point limits were calculated at atmospheric pressure by the Ramsey-Young rule from the boiling curve for n-octane [10].

**All intermediate fractions, which were a mixture of two adjacent normal alkanes, were redistilled and added to the corresponding neighboring fractions. New intermediate fractions were insignificant.

TABLE 5

n-Alkane Content of Fractions with b.p. 190-350° from Petroleums of the Sokolovogorsk and Mirzaan Deposits (in weight percent)

No.	Hydrocarbons	Sokolovogorsk Deposit		Mirzaan Deposit	
		n-alkane content		n-alkane content	
		% in n-alkane mixture	% in starting fraction	% in n-alkane mixture	% in starting fraction
1	n-Undecane	7,0	2,4	3,9	0,3
2	n-Dodecane	8,8	3,1	4,5	0,3
3	n-Tridecane	12,7	4,4	6,0	0,5
4	n-Tetradecane	11,5	4,0	5,5	0,5
5	n-Pentadecane	11,4	4,0	12,2	1,0
6	n-Hexadecane	11,5	4,0	10,9	0,9
7	n-Heptadecane	11,7	4,1	14,5	1,2
8	n-Octadecane	7,1	2,5	14,2	1,2
9	n-Nonadecane	9,9	3,4	13,5	1,2
10	n-Eicosane	8,4	2,9	14,8	1,3

TABLE 6

Motor Properties of Fractions with b.p. 190-350° from Petroleums of the Sokolovogorsk and Mirzaan Deposits

Fraction with b.p. 190-350°	Octane number by motor method*	Cetane number in "Vokesh" motor*	Setting point in °C	Diesel index**	Heating capacity (highest) in cal/kg
Sokolovogorsk deposit, starting	18	46	—20	60,78	10 855
After alkali purification	18	46	—20	—	—
After removal of n-alkanes	28	44	—65	—	10 795
Mirzaan deposit, starting	23	45	—25	51,83	10 754
After alkali purification	23	45	—25	—	—
After removal of n-alkanes	28	43	—70	—	10 828

* Determined in the factory laboratory of the Batumskii Petroleum Processing Plant.

** Calculated from the formula $DH = 2.367\,(t + 17.8)\left(\frac{1.076}{S + 0.004} - 1\right)$, where S is the specific gravity at 20/4, and t is the aniline point.

Calculation of the molar absorption coefficients of the 3.42 μ band from the usual relationship $E = \frac{\log \frac{I_0}{I}}{c \cdot x}$, where c is the concentration in moles per liter (relative to CH_2 groups only) [13], enabled us to obtain the relationship of E to the number of CH_2 groups, as given in Fig. 2.

From Fig. 2, it can be seen that the increase in the value of E is proportional to the number of CH_2 groups, and only in the case of $C_{18}H_{38}$ is the experimental point located beyond the line. Since the spectra of the first alkanes (C_{11}–C_{16}) agrees well with the synthetically prepared C_{11}–C_{16} in a previous investigation by one of us [13], and the intensity of the 3.42 μ band for the other n-alkanes C_{17}–C_{20} increases in proportion to the number of CH_2 groups (Fig. 2, it may be considered that all the normal alkanes separated except n-$C_{18}H_{38}$ were of

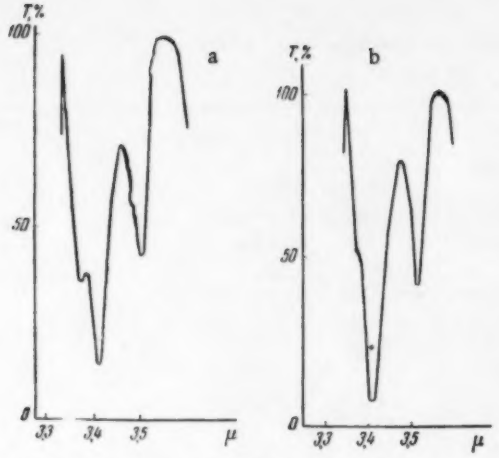


Fig. 1. IR spectra in the 3.3-3.6 μ region: a) n-undecane n-$C_{11}H_{24}$; b) n-eicosane n-$C_{20}H_{42}$.

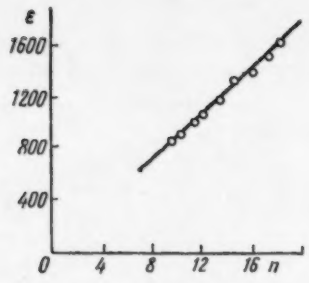


Fig. 2. Relationship of the absorption coefficient of the 3.42 μ band to the number of CH_2 groups (n).

satisfactory purity. However, judging from the molecular refraction of the n-octadecane it also was almost sufficiently pure. To confirm the individual nature of the hydrocarbons separated, we carried out an x-ray analysis of three samples of crystals, namely: 1) urea crystals; 2) the complex of urea with synthetic cetane; and 3) the complex of urea with a mixture of normal alkanes from the fraction of Sokolovogorsk petroleum under investigation.*

The analysis showed that the x-ray structure of the 1st sample differed essentially from the structure of the 2nd and 3rd samples, which gave practically identical x-rays. From this it can be assumed that only n-alkanes enter into the crystal lattice of these complexes.

The n-alkane content of the fractions investigated are given in Table 5.

It also was of interest to determine the parameters characterizing the motor properties of the fractions studied. The data that we obtained are given in Table 6. It appears from the data in this table that the Mirzaan petroleum had somewhat lower properties than the Sokolovogorsk petroleum.

SUMMARY

1. Ten normal alkanes of the composition $C_{11}H_{24}$–$C_{20}H_{42}$ from the fractions of Sokolovogorsk and Mirzaan petroleums with b.p. 190-350° have been identified by physicochemical methods and infrared spectroscopy.

2. The content of each of the hydrocarbons separated in the fractions with b.p. 190-350° has been established.

3. The motor properties of the mixtures of n-alkanes separated have been determined.

LITERATURE CITED

[1] L. M. Rozenberg and N. S. Genekh, Proc. Acad. Sci. USSR 84, 523 (1952).

[2] V. A. Nekrasova and N. I. Shuikin, Proc. Acad. Sci. USSR 97, 843 (1954).

[3] V. A. Nekrasova and N. I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, 950.**

[4] V. G. Nikolaeva, E. V. Zvereva, K. N. Zimina and E. M. Popova, Chemistry and Technology of Fuels 3, 11 (1956).

[5] W. Schlenk, Jr. Analyst 77, 867 (1952).

[6] W. Damazk and K. A. Kobe, Petrolum Refiner 31, No. 3, 106; No. 5, 151 and No. 7, 125 (1952).

* Analysis was carried out in the physical chemistry laboratory of the Institute of Chemistry of the Academy of Sciences of the Georgian SSR by D. D. Sesiashvili, to whom we express our thanks.

** Original Russian pagination. See C. B. Translation.

[7] H.J. Hepp, E. O. Box and G. C. Ray, Ind. Eng. Chem. 45, No. 1, 112 (1953).

[8] D. Swern, Ind. Eng. Chem. 47, No. 2, 216 (1955).

[9] Trans. GrozNII,* Moscow-Leningrad 1931, p. 105.

[10] L. Gurvich, Sci. Bases of Petroleum Processing, Sov. Petr. Indus. Press, Moscow-Leningrad 1931, p. 318.**

[11] B. L. Moldavskii, Proc. Acad. Sci. USSR 1, No. 6-7, 507 (1935).

[12] B. D. Obolentsev, Phys. Constants of Hydrocarbons of Liquid Fuels and Oils, Gostoptekhizdat, 1953, pp. 44-70.**

[13] Iu. P. Egorov and A. D. Petrov, J. Anal. Chem. 9, 483 (1956).***

[14] Kh. M. Minachev, N. I. Shuikin, L. M. Feofanova and Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 352. ***

[15] B. M. Rybak, Analysis of Petroleum and Petroleum Products, Baku Press, Leningrad, 1948, p. 48.**

[16] A. D. Petrov, Chemistry of Motor Fuels, Acad. Sci. USSR Press, Moscow, 1953, p. 93.**

P. G. Melikashvili Institute of Chemistry of the Academy of Sciences of the Georgian SSR and N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences USSR

Received March 22, 1957

*Groz NII = Grozny Petroleum Scientific Research Institute.

**In Russian.

***Original Russian pagination. See C. B. Translation.

CARBON-CHAIN POLYMERS AND COPOLYMERS

5. COPOLYMERIZATION OF ACRYLONITRILE AND METHYL METHACRYLATE IN THE PRESENCE OF TRIBUTYLBORINE

G. S. Kolesnikov and N. V. Klimentova

It has been previously found by one of us and Fedorova [1] that acrylonitrile polymerizes under the influence of tributylborine activated with boron fluoride etherate. Continuing the investigation of the use of tributyl boron as a polymerization catalyst, we have undertaken a study of the copolymerization of acrylonitrile and methyl methacrylate in the presence of this catalyst. It was established by preliminary experiments that methyl methacrylate polymerizes when a solution of it is heated in toluene with tributylborine activated with boron fluoride etherate, but at the same time polymerization of methyl methacrylate proceeds even in the absence of an activator, with only tributylborine present.

The experiments were carried out as follows: to a solution of a mixture of the monomers in toluene, heated to the desired temperature, were added the catalyst and activator, with stirring which was continued for the selected length of time, after which alcohol and water were added and the solvent and unreacted monomers were steam-distilled off; the catalyst was partially decomposed and partially steam-distilled off. The copolymer was filtered out, washed with hot water, and dried at 50-60°. The composition of the copolymer was determined from its average nitrogen content.

The first series of experiments was carried out with the objective of clarifying the effect of the concentration of catalyst and activator on the composition, yield, and properties of the copolymer. In this series of experiments the temperature (60°), the total concentration of monomers in the solvent (0.25 mole in 100 ml of toluene), the molar ratio of the monomers (1 : 1), the duration of the reaction (2 hours), and the molar ratio of the catalyst and activator (1 : 1) were constant; the concentration of catalyst and activator varied. The results of this series of experiments are shown in Table 1.

It can be seen from Table 1 that a rise in the concentration of the catalyst and activator was accompanied by an increase in yield of the copolymer, and this increase was most noticeable when the concentration of catalyst was raised to 2 mole %, with a further rise in the concentration of catalyst resulting in a negligible increase in the yield of copolymer. The composition of the copolymer was practically unchanged when the catalyst concentration was varied; a similar picture was observed by Overberger [2], who found that the relative activity of substituted styrenes did not depend on the concentration of polymerization catalyst. The greatest effect of a change in concentration was on the molecular weight of the copolymer, which was evaluated from the viscosity of solutions of the copolymers in dimethylformamide at 20°. With a rise in the concentration of catalyst, the viscosity of the copolymers at first increased and reached a maximum value at a catalyst concentration of 3.0 mole %, after which the viscosity decreased. Thus, to obtain a copolymer of maximum molecular weight it was necessary to use a catalyst concentration of the order of 2-3 mole % of the total monomers.

It should be kept in mind that the above-mentioned results are from experiments in which the concentrations of catalyst and activator were equal. It is perfectly obvious that the ratio of catalyst and activator concentrations taken could only by chance prove to be optimum, and in order to clarify the effect of the concentration of the activator relative to the catalyst, we carried out a series of experiments in which the total concentration of the monomers (0.25 mole in 100 ml of toluene), the duration of the reaction (2 hours), the reaction temperature (60°), the molar ratio of the monomers (1 : 1), and the concentration of catalyst (2.5 mole % of the total

TABLE 1

Copolymerization of Acrylonitrile and Methyl Methacrylate

Concentration (mole %) of total monomers		Yield of copolymer in % of theor.	[η]	Nitrogen content of copolymer in %	Composition of copolymer in mole %	
tributyl-borine	boron fluoride etherate				acrylo-nitrile	methyl methacrylate
0,5	0,5	4,5	0,045	5,54 5,71	33,3	66,7
1,0	1,0	27,0	0,058	6,50 6,25	39,0	61,0
1,5	1,5	25,2	0,075	5,34 5,93	33,3	66,7
2,0	2,0	45,0	0,095	6,46 6,75	38,6	61,4
2,5	2,5	46,0	0,065	6,39 6,36	39,0	61,0
3,0	3,0	45,0	0,125	5,50 5,77	33,3	66,7
3,5	3,5	55,8	0,030	5,79 5,80	34,6	65,4
4,0	4,0	47,1	0,040	5,40 5,24	32,4	67,6
4,5	4,5	55,8	0,058	5,70 5,64	33,3	66,7
5,0	5,0	48,4	0,015	5,69 5,69	34,2	65,8

TABLE 2

Effect of Activator Concentration on Copolymerization of Acrylonitrile and Methyl Methacrylate

Conc. of activator in mole % of catalyst	Yield of copolymer in % of theor.	[η]	Nitrogen content of copolymer in %	Composition of copolymer (mole %)	
				acrylonitrile	methyl methacrylate
2,0	50,2	0,030	6,07 5,88	33,5	64,5
4,0	52,4	0,048	5,83 6,04	35,5	64,5
6,0	50,5	0,050	5,80 6,02	35,6	64,4
8,5	56,6	0,045	5,57 5,76	34,1	65,9
11,0	57,6	0,060	5,71 5,66	33,3	66,7
12,5	63,3	0,015	5,73 5,67	34,2	65,8
15,0	55,2	0,013	6,03 6,11	35,9	64,1
17,0	59,6	0,035	6,01 5,98	35,6	64,4
30,0	50,0	0,050	6,43 6,59	37,5	62,5
50,0	58,2	0,058	6,45 6,57	37,5	62,5
100,0	39,2	0,033	5,09 5,07	31,0	69,0
150,0	40,6	0,095	5,47 5,44	32,9	67,1

TABLE 3

Effect of Reaction Temperature on Copolymerization of Acrylonitrile and Methyl Methacrylate

Reaction temperature in °C	Yield of copolymer in % of theor.	[η]	Nitrogen content of copolymer in %	Composition of copolymer (mole %)	
				acrylonitrile	methyl methacrylate
20	37,3	0,078	5,01 4,96	30,5	69,5
30	53,6	0,118	5,60 5,52	33,4	66,6
40	48,0	0,120	5,67 5,62	33,7	66,3
50	46,0	0,078	5,59 5,52	33,4	66,6
60	58,3	0,073	5,84 5,74	34,6	65,4
70	55,0	0,040	6,32 6,49	37,6	62,4
80	44,5	0,043	6,27 6,28	37,0	63,0

TABLE 4

Effect of Duration of Reaction on Copolymerization of Acrylonitrile and Methyl Methacrylate

Duration of reaction in hours	Yield of copolymer in % of theor.	[η]	Nitrogen content of copolymer in %	Composition of copolymer in mole %	
				acrylonitrile	methyl methacrylate
0,5	35,6	0,040	5,44 5,71	32,8	67,2
1,0	48,7	0,055	5,87 5,79	34,6	65,4
2,0	57,4	0,073	5,84 5,74	34,6	65,4
3,0	59,7	0,113	6,38 6,32	37,1	62,9
4,0	52,5	0,085	6,02 5,98	35,6	64,4
5,0	62,2	0,095	6,53 6,58	38,2	61,8

monomers) were constant; the concentration of activator was varied from 2 to 150 mole % of the amount of catalyst. The results of this series of experiments are shown in Table 2.

It can be seen from Table 2 that the concentration of activator did not affect the composition of the copolymer and had practically no effect on its yield; it can be noted that at activator concentrations above 30 mole-% some stabilization of the viscosity of the copolymers obtained was observed.

In order to clarify the effect of temperature on the process of copolymerization of acrylonitrile and methyl methacrylate in the presence of tributylborine activated by boron fluoride etherate, we carried out a series of experiments in which the total concentration of monomers (0.25 mole in 100 ml of toluene), the molar ratio of monomers in the mixture (1 : 1), the concentration of catalyst (2.5 mole % of total monomers), the concentration of activator (25 mole % of the catalyst), and the duration of the reaction (2 hours) were constant; the temperature was varied from 20 to 80°. The results of these experiments are shown in Table 3.

TABLE 5

Effect of Ratio of Monomers in Starting Mixture on Copolymerization of Acrylonitrile and Methyl Methacrylate

Comp. of starting mixture of monomers (mole %)		Yield of copolymer in % of theor.	[η]	Nitrogen content of copolymer in %	Composition of copolymer (mole %)	
acrylonitrile	methyl methacrylate				acrylonitrile	methyl methacrylate
100	0	61,5	0,270		100	0,0
90	10	46,5	0,125	16,67 16,93	76,7	23,3
80	20	70,1	0,100	11,64 11,55	59,5	40,5
70	30	45,1	0,075	8,78 8,81	48,4	51,6
60	40	40,0	0,078	7,11 7,28	41,4	58,6
50	50	58,5	0,073	6,45 6,57	38,2	62,8
40	60	66,6	0,030	5,41 4,97	31,3	68,7
30	70	55,0	0,035	3,44 3,53	22,7	77,3
20	80	66,5	0,028	2,43 2,31	15,6	84,4
10	90	74,4	0,010	1,46 1,40	9,9	90,1
0	100	64,0	0,013		0,0	100

It can be seen from Table 3 that at temperatures from 30° up, the yield of copolymers remained practically constant, and the viscosity reached a maximum at 30-40°; further increase in the temperature led to a decrease in viscosity, which is entirely according to rule, since it is known that with a rise in polymerization temperature the molecular weight of the polymer decreases as a result of an increase in the number of centers of initiation of polymerization.

A subsequent series of experiments was carried out to clarify the effect of the duration of the reaction on the course of the process of copolymerization of acrylonitrile and methyl methacrylate. In these experiments the total concentration of monomers (0.25 mole in 100 ml of toluene), the molar ratio of the monomers in the mixture (1 : 1), the temperature (60°), the catalyst concentration (2.5 mole % of the total monomers), and the concentration of activator (25 mole % of catalyst) were constant; the duration of the reaction was varied from 30 min. to 5 hours. The results of the experiments are shown in Table 4.

It can be seen from Table 4 that an increase in the duration of the reaction from 0.5 to 2 hours led to a noticeable increase in the yield of copolymer; further increase in the time had less effect on the yield. The viscosity increased with an increase in the duration of the reaction up to 3 hours, after which the viscosity decreased a little.

It must be noted that the concentration of catalyst and of activator, the temperature, and the duration of the reaction did not affect the composition of the copolymer formed, as can be seen from Tables 1-4. All of the copolymers obtained were readily soluble in acetone and dichloroethane, and poorly soluble in amyl acetate.

We attempted to clarify the effect of the monomer ratio on the course of the process of copolymerization of acrylonitrile and methyl methacrylate in the presence of tributylborine and boron fluoride etherate. For this purpose we carried out a series of experiments in which the total concentration of monomers (0.25 mole in 100 ml of toluene), the temperature (60°), the catalyst concentration (2.5 mole % of the total monomers), the activator concentration (25 mole % of the catalyst), and the duration of the reaction (2 hours) were constant; the acrylonitrile content of the mixture of monomers was varied from 0 to 100%. The results of the experiments are shown in Table 5.

It can be seen from Table 5 that in all cases the acrylonitrile content in the copolymer was lower that in the starting mixture of monomers. This indicates the greater reactivity of methyl methacrylate in the copolymerization reaction in the presence of tributylborine activated with boron fluoride etherate. An increase in the methyl

methacrylate content of the starting mixture of monomers led to a sharp lowering of the viscosity of the copolymer formed, which may be a consequence of rupture of the chain as a result of reaction of the growing polymer radical with the monomeric methyl methacrylate; we have not studied the mechanism of breakage of the chain.

The total concentration of monomers in the reaction mixture was not without effect on the course of the copolymerization process, and with other conditions equal, an increase in the concentration of monomers led to an increase in the yield of copolymer and a rise in its viscosity. Thus, an increase in the total concentration of monomers from 0.125 mole in 100 ml of toluene to 0.50 mole in the same volume of toluene led to an increase in yield of copolymer from 42.1 to 59.7% and an increase in viscosity from 0.038 to 0.063 (temperature 60°, molar ratio of monomers 1:1, concentration of tributylborine 2.5 mole % of total monomers, concentration of boron fluoride etherate 25 mole % of catalyst, duration of experiment 2 hours).

SUMMARY

The copolymerization of acrylonitrile and methyl methacrylate in toluene in the presence of tributylborine and boron fluoride etherate has been studied and the effect of various factors on the course of the copolymerization process has been clarified.

LITERATURE CITED

[1] G. S. Kolesnikov and L. S. Fedorova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 236.*

[2] C. G. Overberger, R. J. Ehrig and D. Tanner, J. Amer. Chem. Soc. 76, 772 (1954).

Institute of Heteroorganic Compounds
of the Academy of Sciences USSR

Received March 21, 1957

*Original Russian pagination. See C. B. Translation.

Brief Communications

THE SYNTHESIS OF NITROMETHANE LABELED WITH RADIOCARBON

P. I. Levin

In the study of the mechanism of oxidation reactions the use of radioactive isotopes opens up new possibilities for the study of the rate of formation and consumption of intermediate products [1] and of the mechanism of homogeneous catalysis [2]. In connection with a study of the mechanism of the nitromethane-initiated oxidation of hydrocarbons, we carried out in the present work the synthesis of $C^{14}H_2NO_2$.

EXPERIMENTAL

Synthesis was carried out by the following steps:

$$C^{14}H_3COOH + Cl_2 \rightarrow C^{14}H_2ClCOOH;$$
$$C^{14}H_2ClCOOH + NaOH \rightarrow C^{14}H_2ClCOONa + H_2O;$$
$$C^{14}H_2ClCOONa + NaNO_2 \rightarrow C^{14}H_2NO_2COONa + NaCl;$$
$$C^{14}H_2NO_2COONa + H_2O \rightarrow C^{14}H_3NO_2 + NaHCO_3.$$

Monochloroacetic acid was synthesized starting from 25 g glacial acetic acid which was prepared with a specific activity of 2.4 mC/mole. The acetic acid was chlorinated in a small flask with a reflux condenser in presence of red phosphorus at the temperature of a boiling water bath. Completion of chlorination was checked by cooling the flask with cold water (the liquid solidified on shaking if chlorination was complete).

Monochloroacetic acid was isolated from the mixture by distilllation.

During distillation the 150-200° fraction was collected. The precipitated crystals were filtered off and the filtrate was again distilled for recovery of the monochloroacetic acid remaining in solution. During redistillation the 170-200° fraction was collected. The isolated monochloroacetic acid was finally purified by redistillation. From 25 g acetic acid was obtained 23 g $ClCH_2COOH$ or 58% of the theoretical yield. 5 g of unreacted acetic acid was recovered and could be used again for synthesis. The boiling point of the monochloroacetic acid was 189.3°; m.p. 61.8°; these values are close to those given in the literature.

For the preparation of nitromethane, the 23 g monochloroacetic acid was placed in a small Wurtz flask, 23 g ice was added, and the mixture was neutralized with 40% sodium hydroxide solution until it had a weakly alkaline reaction (test with phenolphthalein). During neutralization it was necessary to keep the temperature not above 20°, since at higher temperatures some sodium glycolate is formed [3] and reduces the yield of nitromethane. To the solution was then added 15.5 g sodium nitrite dissolved in 23 ml water. The flask was attached to a water condenser, and the solution was heated until reaction started (at 80°). Carbon dioxide came off. Heating was then stopped but the temperature rose to 90° due to the heat of reaction. After the reaction had ceased, the temperature fell and the solution was again heated. Distillation was carried out to 110° for complete separation of the nitromethane from the liquid. The nitromethane came over with water and collected in the receiver as a heavy layer. The latter was separated in a separating funnel. Sodium chloride was added to the aqueous fraction and the nitromethane was distilled off. The combined nitromethane fractions were dried with calcium chloride and redistilled, the 98-101.5° fraction being collected. From 23 g monochloroacetic acid was obtained 4.9 g nitromethane or 33% of the theoretical quantity; on the basis of the acetic acid taken, the yield is 19.1%. The nitromethane had d^{20}_4 1.136 and n^{20}_4 1.382 in agreement with the literature.

The specific activity of the nitromethane was determined by combustion over copper oxide to CO_2 which was then converted to $BaCO_3$. The activity of the latter was measured with an end-type counter. The specific activity was calculated from a nomogram constructed to allow for absorption of electrons by the solid $BaCO_3$ in dependence on its thickness [4]. Results of determination of the specific activity of the $BaCO_3$ are set forth in the table.

TABLE

Weight of solid $BaCO_3$ in mg	Measured activity of $BaCO_3$ in pulses/min	Specific activity of $BaCO_3$ in pulses/min·mg
13.7	2118	670
12.2	2021	660
15.2	2212	680
23.4	2442	780
25.1	2400	710
23.1	2384	710
17.5	2291	690
17.9	2296	690
16.1	2185	660

We see from the table that the mean specific activity of the $BaCO_3$ is 690 pulses/min·mg. Taking the coefficient of efficiency of the counter as 10%, we can calculate the specific activity of the nitromethane from the equation:

$$\alpha = \frac{M_{BaCO_3} \cdot 690 \cdot 10 \cdot 61000}{M_{CH_3NO_2} \cdot 60 \cdot 3{,}7\ 10^7} = 0{,}6 \text{ mC/mole},$$

where M_{BaCO_3} and $M_{CH_3NO_2}$ are the molecular weights of barium carbonate and nitromethane. Since the nitromethane used for the determination of specific activity was diluted 3.7 times with nonradioactive material, the specific activity of the synthesized nitromethane is equal to 22.2 mC/mole. The total activity of the synthesized CH_3NO_2 is $I = \frac{4.9 \times 2.22}{61} = 0.18$ mC; on the basis of the original total activity of the acetic acid, the activity of the nitromethane is 1 mC; the activity yield for the synthesis of nitromethane is therefore 18%.

The yield of nitromethane from acetic acid (19.1%) and the total radioactivity yield are therefore nearly the same.

SUMMARY

1. A method was developed for preparation of nitromethane labeled with radiocarbon, starting from acetic acid labeled in the methyl group.

2. The specific activity of the synthesized nitromethane was measured, and it was shown that the yield of nitromethane from acetic acid is the same as the total radioactivity yield of the prepared nitromethane.

Institute of Chemical Physics
of the Academy of Sciences of the USSR

Received April 4, 1958

LITERATURE CITED

[1] M. B.Neiman, J. Phys. Chem. 28, 1235 (1954).

[2] N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity [in Russian] (Acad. Sci. USSR Press, Moscow, 1954).

[3] Synthesis of Organic Preparations [Russian translation] (For. Lit. Press, Moscow, 1949), Vol. 1, p. 303.

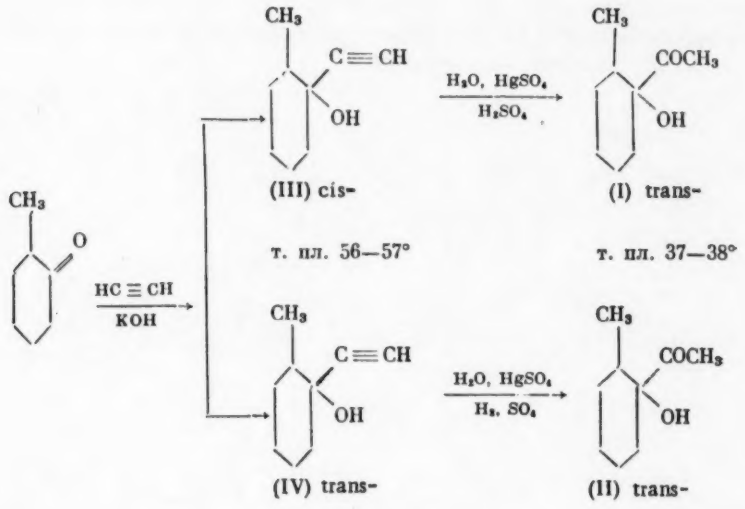
[4] Preparation and Determination of Labeled Atoms [Russian translation] (For. Lit. Press, Moscow, 1948).

RAMAN SPECTRUM INVESTIGATION OF THE CONFORMATIONS OF CIS- AND TRANS-1-ACETYL-2-METHYLCYCLOHEXANOLS

M. I. Batuev, A. A. Akhrem, A. D. Matveeva and I. N. Nazarov

In the chair-form of cyclohexane (in which it mainly exists) each carbon atom is known to possess one equatorial and one axial C−H bond; the ring contains six equatorial (e) and six axial (a) C−H bonds. In substituted cyclohexanes the position of the substituents (axial or equatorial) influences the physical properties, in particular the bond energies, the vibration frequencies, and the interatomic distances of the atoms in the substituent groups. In addition the conformation of the substituent influences the reactivity of the later [1, 2].

In the present work we made an optical investigation of the conformation of the epimeric 1-acetyl-2-methylcyclohexanols (I) and (II) obtained by hydration of the corresponding 1-ethynyl-2-methylcyclohexanols (III) and (IV) [2]:



EXPERIMENTAL

The physical properties of 1-acetyl-2-methylcyclohexanols (I) and (II) are set forth in the table.

The Raman spectra were plotted in the liquid phase using an ISP-51 3-prism spectrograph (Russian manufacture) and the exciting blue 4358 A line of a mercury vapor lamp;*

*Intensity symbols: b broad line, s sharp line, d doublet; the asterisks refer to lines arranged with a background common to neighboring lines denoted by the same number of asterisks.

TABLE

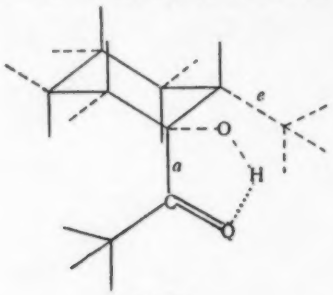
Physical Properties of the 1-Acetyl-2-methylcyclohexanols (I) and (II)

Compound	B.p. in °C (p in mm mercury)	M.p. in °C	d_4^{20}	n_D^{20}	*MR* found	*MR* calculated
Cis-1-acetyl-2-methyl-cyclohexanol (I)	92—93 (8)	37—38	1,0226	1,4735	42,83	43,10
Trans-1-acetyl-2-methyl-cyclohexanol (II)	82—83 (10)	—	0,9974	1,4620	43,00	43,10

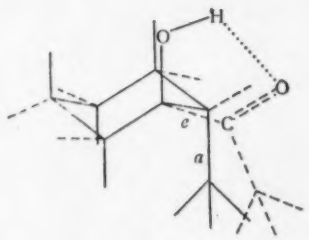
I. Cis-1-acetyl-2-methylcyclohexanol, $\Delta\nu$ cm^{-1}: 182(2•), 195 (2•), 252 (0), 265 (0), 338 (2), 411 (1•), 424(1•), 437(2•), 451(2•), 507(1), 534(1), 547(2•), 561(2•), 598(3), 618(0), 649(4), 690(4), 795(1), 810(2s), 837(2s), 857(1•), 874(1•), 965 (3••), 982(3••), 1002(4•), 1012(4•), 1034(1), 1060(3•), 1074(3•), 1088(3•), 1118(2••), 1136(2••), 1156(2••), 1171(2••), 1208(2), 1224(2), 1261(4•), 1274(5•), 1300(2••), 1315(2••), 1332(1••), 1345(2••), 1361(2••), 1442(7• d), 1457(3•), 1468(4•), 1691(4••), 1702(2••), 1713(1••), 2861(6•), 2886(1•), 2899(2•), 2915(10•), 2929(10•), 2943(9•), 2954(4•), 2975(4•), 3010(2•), 3394-3524(3, band).

II. Trans-1-acetyl-2-methylcyclohexanol, $\Delta\nu$ cm^{-1}: 166(3•), 180(3•), 256(3•• b, d), 271(2••), 291 (0), 303(0•), 317(2• b, d), 377(2••), 387(2••), 397(2••), 426(4), 475(4), 511(3), 556(3d), 602(4 b), 692(10b), (10), 807(4), 825(5), 859(4), 895(2•), 910(2•), 965(5), 992(5), 1016(5), 1067(6), 1092(3), 1132(4), 1152(5•), 1164(5•), 1213(4), 1233(4), 1268(6 b), 1333(4•), 1351(4•), 1439(9••), 1451(9••), 1465(9••), 1704(7), 2656 (1•), 2673(1•), 2690(1•), 2717 (1••), 2753(1••), 2858(6•), 2897(2•), 2919(6•), 2929(10•), 2943(10•), 2976 (4•), 3013(2•), 3450-3509 (4, band).

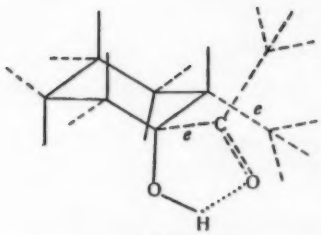
Conformations are usually governed by the relative positions of the largest substituents (in this case the acetyl and methyl groups). In the case of the chair-shaped cyclohexane ring* we can distinguish between two cis- and two trans-conformations of the investigated compounds:



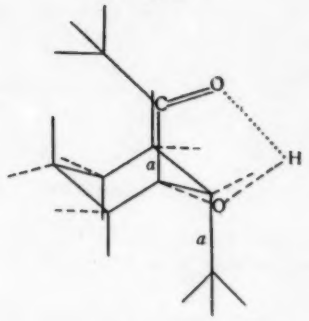
cis, ae



cis, ae



trans, ee



trans, aa

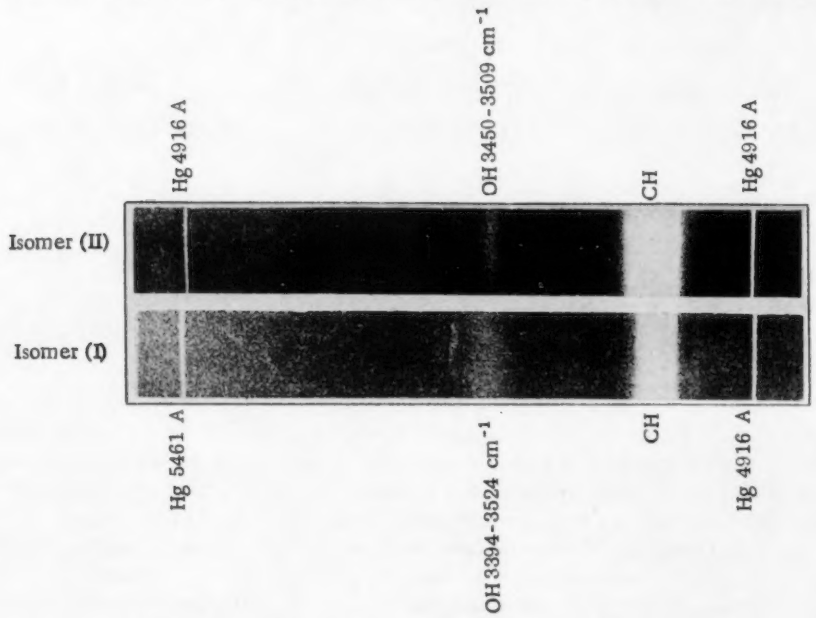
*This form predominates at room temperature; the tautomeric mixture contains an extremely small amount of the boat-shaped form whose contribution increases with rising temperature.

We have to consider which of these conformations predominates in the investigated compounds.

The pulsating frequency of the ring vibrations of the trans-form of ortho-substituted cyclohexanes is usually higher than that of the cis-form [1]. In compound (II) this frequency is 692 cm^{-1}; in (I) it is 649 cm^{-1}. Hence, as indicated above, compound (I) is the cis-form and compound (II) the trans-form. But whereas the spectrum of (II) contains no trace of the 649 cm^{-1} frequency, the spectrum of (I) contains both the 649 cm^{-1} and the 690 cm^{-1} frequencies with similar intensities. It is therefore probable that compound (I) has conformations, apart from the pulsating ring vibration frequency of 649 cm^{-1}, characterized by the 690 cm^{-1} pulsating ring vibration. The cause of this may be the admixture of compound (II) and other possible conformations with the same frequency of the ring pulsating vibration. The presence of (I) in admixtures of other conformations is evidently due to the spectrum of (I) (m.p. 37-38°) being plotted in the fused, supercooled state (at 25°) in which reciprocal transitions of the predominant conformation into other conformations could occur.

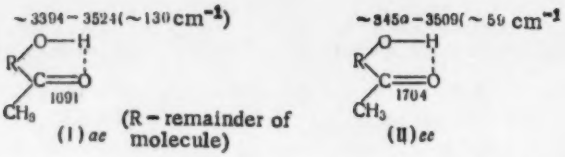
This hypothesis is also supported by data for the C=O bond frequencies. In the spectrum of compound (II) the C=O frequency is represented by one line at 1704 (7) cm^{-1}, in the spectrum of compound (I) it is represented by three lines at 1691 (4), 1702 (2) and 1713 (1) cm^{-1}. The strongest of these (1691 cm^{-1}) characterizes the predominant conformations of compound (II); the other two characterize the other conformations including also compound (II). According to earlier work [1, 3] the higher frequency of the C=O bond in the predominating conformation of (II) (1704 cm^{-1}) in comparison with that of the C=O bond in the predominant conformation of compound (I) indicates that the acetyl group in (II) is in the equatorial position (conformation ee), while in the predominating conformation of (I) it is in the axial position (ae).

These conclusions are also supported by data for the hydroxyl group frequencies. In both of the compounds the hydroxyl group is associated with an intramolecular hydrogen bond, as is reflected in marked narrowing of the hydroxyl band [4], especially in compound (II) (approx. 59 cm^{-1}). In compound (II) it is more than twice as broad (approx. 130 cm^{-1}), and the edge on the lower frequency side (at about 3394 cm^{-1}) for compound (I) is 56 cm^{-1} lower than for compound (II) at about 3450 cm^{-1} (see diagram). According to [1] this points to a more acidic character of the hydroxyl of the predominant conformation of compound (I) in comparison with compound



Raman spectra of cis- and trans-2-methyl-1-acetylcyclohexanols.

(II), and in turn indicates that its position in (I) is equatorial and that in (II) it is axial. We may note that the greated acidity of the hydroxyl group of the predominant conformation ae of compound (I), due to the stronger hydrogen bond with the C=O bond, brings about more considerable lowering of the frequency of the latter (i.e., greater increase of length and greater lowering of energy) than in the conformation of compound (II).



(I) *ae* (R – remainder of molecule) (II) *ee*

On the basis of experiments on the acetylation of the isomeric 1-acetyl-2-methylcyclohexanols (I) and (II), two of us [2] and [5] formulated the theory of the equatorial position of the hydroxyl group in the cis-isomer (I) and of the axial position in the trans-isomer (II). This proposal was put forward after it had been found that compound (I) acetylates under milder conditions than compound (II). The present work coupled with [1] has confirmed the theory and has supplied physical evidence for the findings.

SUMMARY

The cis-configuration of 1-acetyl-2-methylcyclohexanol exists in the form of the predominant ae conformation; the trans-configuration in the form of the ee conformation.

Institute of Combustible Minerals
of the Academy of Sciences USSR
and the N. D. Zelinskii Institute of
Organic Chemistry of the Academy of Sciences USSR

Received April 8, 1958

LITERATURE CITED

[1] M. I. Batuev, A. A. Akhrem, A. D. Matveeva and I. N. Nazarov, Proc. Acad. Sci. USSR,* 117, 423 (1957); 120, 779 (1958).

[2] I. N. Nazarov and A. A. Akhrem, J. Gen. Chem.,* 28, 1791 (1958).

[3] D. Barton and R. Cookson, Quart. Rev. 10, 44 (1956).

[4] M. I. Batuev, Proc. Acad. Sci. USSR 28, 423 (1940); 40, 315 (1943); 47, 10 (1945).

[5] J. Pasquel, I. Sistare and A. Regas, J. Chem. Soc. 1949, 1943; H. Orloff, Chem. Rev. 54, 347 (1954).

THE RAMAN SPECTRUM OF HEXACHLOROBUTADIENE

M. I. Batuev and A. D. Matveeva

Hexachlorobutadiene – $Cl_2C=C(Cl)-(Cl)C=CCl_2$ – cannot exist in a plane cis form since two of its four terminal chlorine atoms would then approach to a distance of about 1.7 A, whereas in the chlorine molecule (Cl_2) the interatomic distance is 1.98 A [1]. The nonexistence of a cis form is also supported by chemical facts: hexachlorobutadiene does not enter into the diene synthesis, and it is well known that this reaction requires the diene to be in the cis form [2]. Energetic and other considerations point to a probable nonplanar character of the molecule: one-half of the molecule is evidently removed from the plane cis form by about 82°; the system then possesses a minimum of potential energy [1]. It was of interest to clarify the influence of the conjugated double bonds in hexachlorobutadiene on some aspects of the structure of this molecule.

The CC bonds of ethane, ethylene and acetylene are usually taken as standards in investigations of hydrocarbon molecules containing conjugated multiple bonds. The bond orders in ethane, ethylene and acetylene are

*Original Russian pagination. See C. B. Translation.

assumed to be respectively 1, 2 and 3 [3]: the CC bond lengths decrease with increasing bond order, and their vibration frequencies and energies increase (Table 1).

TABLE 1

CC bond	Unit of measurement	H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$
Order [3]	Arbitrary units	1	2	3
Length [4]	in Å	1,55	1,353	1,205
Vibration frequencies [5]	cm^{-1}	992	1621	1974
Energy [6]	kcal/mole	83	110	145

TABLE 2

CC bond	Unit of measurement	Cl_3C-CCl_3	$Cl_2C=CCl_2$
Order	Arbitrary units	1	2
Length [4]	in Å	....	1,38
Vibration frequency [5]	cm^{-1}	854	1571

Due to the specific characteristics of multiple bonds, the above-noted interdependent change in their parameters follows a regular trend: increase in energy of these characteristic bonds is always accompanied by decrease in their length and increase in their vibration frequencies; conversely, decrease of their energy is always associated with increase in bond length and decline of their vibration frequencies. The pattern of these changes in certain parameters enables us to evaluate other parameters if no direct data for the latter are available or if existing data are lacking in accuracy [7]. In this connection especially accurate measurements of vibration frequencies can be made by modern optical techniques, and these measurements can serve as a basis for evaluation of various parameters such as bond lengths and energies.*

The foregoing remarks are of course also applicable to the systems $Cl_2C=C(Cl)-(Cl)C=CCl_2$, $Cl-C\equiv C-C\equiv C-Cl$ which are characterized by the C=C and C≡C bonds. As standards of comparison we can here take hexachloroethane (Cl_3C-CCl_3), tetrachloroethylene ($Cl_2C=CCl_2$) and dichloroacetylene ($ClC\equiv CCl$). Complete data for the CC bond parameters in these compounds, such as were cited above for hydrocarbon molecules are not available. Existing data for the CC bonds of hexachloroethane and tetrachloroethylene are presented in Table 2.

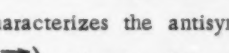
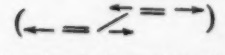
*The carbon atoms in C=C and C≡C bonds, for example, are already very close together; any further decrease in separation distance would affect the forces of repulsion which increase sharply with reduction in interatomic distance. Due to this, the curve of vibration frequencies (ordinate) rises steeply with decreasing separation distance (abscissa) in the C=C and C≡C systems. A considerable rise in the vibration frequencies of these bonds (especially C≡C bonds) accompanies only a minute decrease in interatomic distance, whose direct measurement would be difficult at the present stage of development of the appropriate measuring techniques due to the fact that the magnitude of the decrease is within the limits of experimental error. On the other hand, optical measurements of vibration frequencies in these cases lie well outside the limits of experimental error; for example, the C≡C vibration frequency of diacetylene is 209 cm^{-1} higher than that of acetylene, and the possible error of measurement of these frequencies is only of the order of 3 cm^{-1}. Reliable conclusions about the true changes of length of these bonds can accordingly be drawn by direct physical measurements.

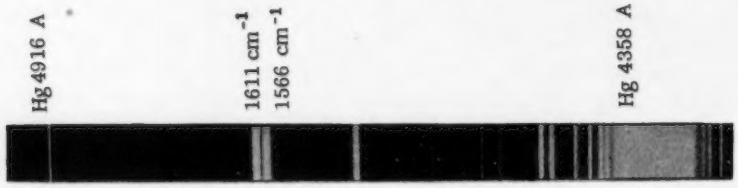
Inspection of the two tables reveals that chlorine atoms lengthen the C−C and C=C bonds in hexachloroethane and tetrachloroethylene in comparison with ethane and ethylene. They also lower the vibration frequencies and consequently the energies of these bonds.

EXPERIMENTAL

The literature for $Cl_2C=C(Cl)-(Cl)C=CCl_2$ is lacking in any data for the CC bond lengths. We plotted the Raman spectrum of this compound, using the Russian ISP-5 spectrograph with a central chamber, with the exciting blue 4358 A line and the violet 4047 A line of the mercury vapor lamp.*

$\Delta\nu$ cm^{-1}: 77(5), 126(4b), 177(4), 200(7), 239(6), 287(2*), 298(5*), 378(5**), 389(5**), 427(10), 564(2*)-578(2*)-585(3*)-594(3*) (lines in a band), 657(5s), 781(1*), 793(3*), 807(1*), 855(4), 942(3), 983(3b), 1170 (6*), 1183(2*), 1566(7b), 1611(10b), 1711(0), 1880(1), 1962(1d).

Natural frequencies and overtones: 585 (287 + 298), 594(298 x 2), 855(427 x 2), 1711(855 x 2), 1880(942 x x 2), 1962(983 x 2), etc. (see diagram). This spectrum confirms that previously published [1] but includes an additional series of lines in the shape of principal frequencies as well as natural frequencies and overtones (564, 578, 594, 781, 1183, 1711, 1880, 1962). The most striking feature of this spectrum is the appearance of two frequencies in the double-bond region which points to interaction of the double bonds − 1566 and 1611 cm^{-1}. The first of these characterizes the antisymmetric  , the second the symmetric  vibration of the double bonds. Whereas the frequency of the antisymmetrical C=C vibration in hexachlorobutadiene (1566 cm^{-1}) is at the level of the C=C vibration in tetrachloroethylene (1571 cm^{-1}), the frequency of the symmetrical vibration in hexachlorobutadiene (1611 cm^{-1}) very considerably (by 40 cm^{-1}) exceeds the C=C vibration frequency in tetrachloroethylene; it also exceeds the mean (1589 cm^{-1}) of the two vibration frequencies (by 18 cm^{-1}). This indicates that in hexachlorobutadiene the C=C bonds are evidently considerably shorter than the C=C bonds in tetrachloroethylene. The C−C vibration frequency in hexachlorobutadiene (1170 cm^{-1}) is considerably higher than in hexachloroethane (854 cm^{-1}), i.e., the central single C−C bond in hexachlorobutadiene is likewise much shorter than the single bond in hexachloroethane.



SUMMARY

The conjugation of the two double bonds in hexachlorobutadiene leads to shortening of the C−C and C=C bonds, i.e., to a certain contraction of the whole molecule.

Institute of Combustible Minerals of
the Academy of Sciences USSR

Received April 8, 1958

LITERATURE CITED

[1] K. Kohlrausch and H. Wittek, Ber. 75, 227 (1942).

[2] O. Fruhrith, Ber. 74, 1700 (1941).

*Intensity designations: b broad line, s sharp line, d doublet; the asterisks denote lines positioned against a background common to neighboring lines which are designated by the same number of asterisks.

[3] C. Coulson, Valence, Oxford, 1953, Proc. Roy. Soc. A 207, 91 (1951); A 169, 413 (1939); State of the Theory of Chemical Structure in Organic Chemistry. Report of the Committee of the Chemical Division of the Academy of Sciences of the USSR [in Russian] (Acad. Sci. USSR Press, 1954).

[4] P. Allen and E. Sutton, Acta Cryst. 3, 46 (1950).

[5] K. Kohlrausch, Raman Spectra [Russian translation] (For. Lit. Press, Moscow, 1952).

[6] T. Cottrell, The Strength of Chemical Bonds [Russian translation] (For. Lit. Press, Moscow, 1952).

[7] M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1956, 1329; J. Gen. Chem.* 26, 1888 (1956); 27, (876 (1957), etc.

REACTIONS OF TRIALKYL PHOSPHITES WITH NITROSYL AND NITRYL CHLORIDES

B. A. Arbuzov and E. N. Ukhvatova

Interaction of trialkyl phosphites with nitrosyl chloride or nitryl chloride would be expected to lead to the interesting products (I) and (II) if the Arbuzov rearrangement occurred:

$$(RO)_3P + NOCl \rightarrow (RO)_2P(=O)-N=O + RCl; \quad (I)$$

$$(RO)_3P + NO_2Cl \rightarrow (RO)_2P(=O)-NO_2 + RCl. \quad (II)$$

It is known that nitrosyl chloride can bring about not only nitrosation but also oxidation or chlorination [1]. Similar reactions can be expected with nitryl chloride [2].

Experiments on reaction of trialkyl phosphites with nitrosyl or nitryl chloride show the predominating reaction course to be oxidation of the trialkyl phosphites to the corresponding phosphates. Reaction of triethyl phosphite with nitryl chloride gives, apart from triethyl phosphate, a small fraction with the constants and analysis of tetraethyl pyrophosphate. Nitrosyl chloride gave a similar fraction but with a lower phosphorus content. Pyrophosphates could not be isolated after reaction of higher alkyl phosphites since decomposition of the high-boiling products takes place during distillation.

Pyrophosphate is probably formed by the following mechanism: Nitrosyl or nitryl chloride oxidizes triethyl phosphite to triethyl phosphate and chlorinates some of the triethyl phosphite to diethylphosphoryl chloride. The latter reacts with triethyl phosphate to give tetraethyl pyrophosphate:

$$(RO)_3P + Cl_2 \rightarrow (RO)_2P(=O)-Cl + RCl,$$

$$(RO)_2P(=O)-Cl + RO-P(=O)(-OR)_2 \rightarrow (RO)_2P(=O)-O-P(=O)-(OR)_2 + RCl.$$

EXPERIMENTAL

Action of nitrosyl chloride on triethyl phosphite. Nitrosyl chloride [3] (10.5 g) was passed into 26.6 g triethyl phosphite in an Arbuzov flask. An exothermic reaction took place. Toward the end the reaction mixture was heated 1 hr on a water bath. Distillation gave 14.3 g (49.1% of theory) of golden yellow triethyl phosphate

*Original Russian pagination. See C. B. Translation.

with b.p. 62.5-63° (1 mm); $n^{20}D$ 1.4054; d^{20}_0 1.0726; found MR 41.66; calculated MR 42.42; calculated M 182.2; found M 182.0 (by cryoscopic determination in benzene).

Found %: P 17.0; C 40.45; H 8.40. $C_6H_{15}O_4P$. Calculated %: P 17.02; C 39.54; H 8.29.

From the higher fractions was separated 2 g of compound with b.p. 131° (1 mm), $n^{20}D$ 1.4182; d^{20}_0 1.1576; calculated for $C_8H_{20}O_7P_2$: P 21.37%; found P 19.92%.

Action of nitryl chloride on triethyl phosphite. 6.3 g nitryl chloride [4] was passed into 13 g of triethyl phosphite. An exothermic reaction took place. Toward the end of the reaction the flask was heated 1 hr on a water bath. Distillation gave 9 g (63.3% of theory) triethyl phosphate with b.p. 66.5-67° (0.5 mm); $n^{20}D$ 1.4052; d^{20}_0 1.0760; found Mr 41.52; found M 184.0 (by cryoscopy in benzene); found P 17.11%. In addition the higher fractions yielded a little tetraethyl pyrophosphate with b.p. 128° (1.5 mm); $n^{20}D$ 1.4207; found P 21.36%.

Action of nitrosyl chloride on tripropyl phosphite. Nitrosyl chloride (19 g) was passed into 60.4 g tripropyl phosphite. After conclusion of the exothermic reaction, the mixture was heated 1 hr on a water bath. Distillation then yielded 40.6 g (62.4% of theory) tripropyl phosphate with b.p. 87.5-88° (1.5 mm); $n^{20}D$ 1.4173; d^{20}_0 1.0091; found MR 55.93; calculated for $C_9H_{21}O_4P$: MR 56.27; found M 227.8; calculated M 224.3.

Found %: C 49.40; H 9.66; P 14.19. $C_9H_{21}O_4P$. Calculated %: C 48.19; H 9.43; P 13.83.

Action of nitrosyl chloride on tributyl phosphite. Nitrosyl chloride (13.6 g) was passed into 51.9 g tributyl phosphite. After completion of the exothermic reaction, the product was heated on an oil bath for 1 hr to 150-180°. Distillation gave 28.6 g (55.2% of theory) of tributyl phosphate with b.p. 105.5-106° (0.5 mm); $n^{20}D$ 1.4265; d^{20}_0 0.9835; found MR 69.46; calculated for $C_{12}H_{27}PO_4$: MR 70.13; found M 259.2; calculated M 266.4.

Found %: C 54.54; H 10.30; P 11.71. $C_{12}H_{27}PO_4$. Calculated %: C 54.10; H 10.21; P 11.67.

Action of nitryl chloride on tributyl phosphite. An exothermic reaction occurred when 18.2 g nitryl chloride was passed into 55.8 g tributyl phosphite. Toward the end of the reaction the flask was heated 2 hr at 130-150°. Distillation gave 40 g (50.9% of theory) tributyl phosphate with b.p. 105.5-106.5° (0.5 mm); $n^{20}D$ 1.4278; d^{20}_0 0.9891; found MR 69.25; calculated for $C_{12}H_{27}O_4P$: MR 70.13; found P 11.53%.

SUMMARY

1. Treatment of trialkyl phosphites with nitrosyl or nitryl chloride led to oxidation to trialkyl phosphates.

2. The reaction of triethyl phosphite in both cases also yielded a small quantity of tetraethyl pyrophosphate.

A. M. Butlerov Institute of Chemical Research
and V. I. Ulianov-Lenin Kazan State University

Received April 26, 1958

LITERATURE CITED

[1] L. J. Beckham, W. A. Fessler and M. A. Kise, Chem. Rev. 48, 353 (1951); A. P. Terent'ev and L. A. Ianovskaia, Reactions and Methods of Investigation of Organic Compounds [in Russian] (Moscow, 1957), vol. 6, p. 75.

[2] M. J. Collis, F. P. Gintz, D. R. Goddard, E. A. Hebdon and G. F. Minkoff, J. Chem. Soc. 1958, 438.

[3] L. Vanino, Handbuch der praparativen Chemie, vol I, 1925, p. 170.

[4] Handbook of Preparative Inorganic Chemistry, edited by G. Brauer [Russian translation] (For. Lit. Press, Moscow, 1956), p. 253.

PREPARATION OF ORGANOSILICON KETONES BY THE DRY DISTILLATION OF SALTS OF ORGANOSILICON ACIDS

D. N. Andreev and E. V. Kukharskaia

Condensation of salts of organic acids is extensively used in organic chemistry for the preparat on of diverse ketones. This reaction has not previously been used, however, for the preparation of organosilicon ketones. We tested the possibility of carrying out this reaction with organosilicon acids by heating calcium salts of trimethylsilylpropionic acid (I) and methyldiethylsilylpropionic acid (II). It was found that the reaction leads to symmetrical silicoketones when starting from salts of organic silicon acids, and to unsymmetrical ketones when starting from mixtures of salts of organosilicon and organic acids. Dry distillation of the calcium salts of acids (I) and (II), for example, gives 22.8 and 28.3% yields respectively of the symmetrical ketones 2,2,8,8-tetramethyl-2,8-disilanonanone-5 (III) and 3,9-dimethyl-3,9-diethyl-3,9-disilaundecanone-6 (IV).

$$[R_3SiCH_2CH_2COO]_2Ca \rightarrow R_3SiCH_2CH_2COCH_2CH_2SiR_3 + CaCO_3.$$

Heating of a mixture of the calcium salt of one of these acids with the calcium salt of isobutyric acid gave the unsymmetrical ketones – 2,2,6-trimethyl-2-silaheptanone-5 (V) (yield 13%) and 3,7-dimethyl-3-ethylsilaoctanone-6 (VI) (yield 15.7%):

$$[R_3SiCH_2CH_2COO]_2Ca + [(CH_3)_2CHCOO]_2Ca \rightarrow 2R_3SiCH_2CH_2COCH(CH_3)_2 + 2CaCO_3.$$

In the latter case the unsymmetrical ketones were accompanied by the symmetrical silicoketones (III) and (IV) and diisopropyl ketone. The investigation established that γ-silicoorganic acids behave in this reaction like organic acids and that distillation of their calcium salts gives ketones in yields of the same order as in the case of organic acids.

EXPERIMENTAL

2,2,8,8-Tetramethyl-2,8-disilanonanone-5 (III). 30 g (0.09 mole) calcium salt of acid (I) was heated in a glass retort to give 16.2 g brown liquid. This was fractionated in vacuo and gave 6.0 g (yield 22.8%) of ketone (III) with b.p. 112-113° (6 mm); $n^{20}D$ 1.4447; d^{20}_4 0.8490; found MR 72.19; calculated MR 72.32. The 2,4-dinitrophenylhydrazone had m.p. 143°.

Found %: N 13.57; 13.71; Si 13.66; 13.77. $C_{17}H_{30}Si_2O_4N_4$. Calculated %: N 13.64; Si 13.67.

3,9-Dimethyl-3,9-diethyl-3,9-disilaundecanone-6 (IV). 45.6 g (0.12 mole) calcium salt of acid (II) was heated in a retort. There was obtained 22.0 g colored condensate. Fractionation gave 9.8 g (yield 28.3%) of ketone (IV) with b.p. 146-149° (2 mm); $n^{20}D$ 1.4573; d^{20}_4 0.8618; found MR 90.71; calculated MR 90.84. The 2,4-dinitrophenylhydrazone had m.p. 82-83°.

Found %: N 12.47; 12.45; Si 12.04; 12.08. $C_{21}H_{38}Si_2O_4N_4$. Calculated %: N 12.00; Si 12.03.

2,2,6-Trimethyl-2-silaheptanone-5 (V). A mixture of 32.8 g (0.1 mole) calcium salt of acid (I) and 64.2 g (0.3 mole) calcium salt of isobutyric acid was heated in a retort. Fractionation of the 29.8 g of condensate gave 6 g (yield 18%) of diisopropyl ketone, 6.7 g (yield 29%) of ketone (III) and 4.6 g (yield 13%) of ketone (V). The latter had b.p. 62-64° (8 mm); $n^{20}D$ 1.4312; d^{20}_4 0.8442; found MR 52.86; calculated MR 53.43. The 2,4-dinitrophenylhydrazone has m.p. 80-82°.

Found %: N 16.00; 15.81; Si 7.68; 7.50. $C_{15}H_{24}SiO_4N_4$. Calculated %: N 15.89; Si 7.96.

3,7-Dimethyl-3-ethyl-3-silaoctanone-6 (VI). A mixture of 38.5 g (0.1 mole) calcium salt of acid (II) and 64.2 g (0.3 mole) of calcium isobutyrate was heated in a retort to give 38.3 g liquid condensation products. Fractionation gave 12.1 g (yield 36.3%) diisopropyl ketone, 3.9 g (yield 13.6%) ketone (IV) and 6.3 g (yield 15.7%) ketone (VI) with b.p. 102.5-104° (8 mm); $n^{20}D$ 1.4496; and d^{20}_4 0.8498; found MR 63.31; calculated MR 62.69. The 2,4-dinitrophenylhydrazone melted at 89°.

Found %: N 14.70; 14.55; Si 7.47; 7.21. $C_{17}H_{28}SiO_4N_4$. Calculated %: N 14.71; Si 7.37.

SUMMARY

1. Dry distillation of the calcium salts of γ-silicoorganic acids can be employed for the synthesis of silicoketones with a symmetrical structure.

2. Unsymmetrical silicoketones can be obtained by dry distillation of a mixture of the calcium salts of silicoorganic and organic acids.

Institute of Silicate Chemistry of
the Academy of Sciences of the USSR

Received May 13, 1958

REACTION OF TRIALKYL PHOSPHITES WITH PHOSGENE

M. I. Kabachnik and P. A. Rossiiskaia

In the No. 1, 1957, issue of this journal our paper on the "Reaction of chloroacetyl chloride, trichloroacetyl chloride and phosgene with trialkylphosphites" was published. In that paper we reported that the reaction of phosgene with trialkyl phosphites gave chloroformylphosphinic esters $ClCOPO(OCH_3)_2$ [1]. These results were not confirmed when the reaction was repeated. In fact, reaction of phosgene with trimethyl phosphite leads to release of carbon monoxide with formation of dimethyl chlorophosphate:

$$COCl_2 + P(OCH_3)_3 = CH_3Cl + CO + ClPO(OCH_3)_2.$$

Since the reaction did not lead to the previously reported chloroformylphosphinic ester, the nature of the products of the subsequent transformations (described in the same paper) also does not correspond to the formulas put forward and remains obscure.

A stream of dry chlorine was passed into 24.8 g (0.2 mole) trimethyl phosphite at −5 to −8° until the odor of the phosphite disappeared. Fractionation in vacuo gave 17.6 g of a substance with b.p. 65-67° (11 mm); $n^{20}D$ 1.4167; d^{20}_4 1.3286; found MR 27.34; calculated MR 27.03.

Found %: C 16.66; 16.72; H 4.32; 4.35; P 21.07; 21.14. $C_2H_6PO_3Cl$. Calculated %: C 16.61; H 4.15; P 21.47.

Literature data for dimethyl chlorophosphate [2]: b.p. 60° (4 mm). Dimethyl anilinophosphonate, prepared by the usual method, had m.p. 88-89°.

Found %: C 48.18; 47.97; H 6.00; 6.13; P 15.46; 15.21. $C_9H_{12}PO_3$. Calculated %: C 47.76; H 5.96; P 15.43.

A mixture with authentic dimethyl anilinophosphonate did not give a depression of melting point (88.5-89°) [3].

Institute of Heteroorganic Compounds
of the Academy of Sciences of the USSR

Received July 4, 1958

LITERATURE CITED

[1] M. I. Kabachnik and P. A. Rossiiskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 48.*

[2] G. M. Kosolapoff, Organophosphorus Compounds, N. Y., J. Wiley; London, Chapman and Hall, 1950, 242.

[3] H. McCombie, B. C. Saunders and G. J. Stacey, J. Chem. Soc. 1945, 921.

*Original Russian pagination. See C. B. Translation.

CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES USSR. MAY 22-23, 1958

On May 22-23, 1958 a regular general meeting of the Division of Chemical Science of the Acad. Sci. USSR was held in the conference hall of the Organic Chemistry Institute of the Acad. Sci. USSR. The meeting was opened by Academician-secretary of the Division of Chemical Science, Acad. N. N. Semenov. He devoted his introductory speech to the historic decisions of the May Plenum of the CC CPSU.* Pointing out that: "This decision surpasses all our expectations; it is a great day for chemistry, but it places also a heavy responsibility on all of our nation's chemists . . .," Acad. N. N. Semenov reported to the general meeting on the work already conducted by this Section and the Presidium of the Academy of Sciences and mentioned some of the more important problems still to be solved. It is necessary to help the industry in getting acquainted more rapidly with the things already accomplished abroad, but we should not be satisfied with this alone. The main purpose of the Academy of Sciences is to create new projects, search for new routes, new scientific and technological possibilities. Particular attention should be given to the problems of organizing properly the introduction of scientific achievements into industry. Without a solution of this problem on a national scale it is impossible to achieve any great success. It is necessary to strengthen the ties with business concerns and Councils of National Economy, and organize pilot plants at the Academy of Sciences. Having put forth the actual problems facing each institute of the Section, the speaker called on every worker in the institute to participate actively in solving these problems.

The speech of the Section's Academician-secretary received a wide response. Some concrete proposals for a series of problems were put forth by Academicians: A. V. Topchiev, S. I. Vol'fkovich, A. N. Frumkin, M. M. Shemiakin, Corresponding Members Acad. Sci. USSR: N. I. Nikitin, I. A. Kazarnovskii, S. Z. Roginskii, Dr. Chem. Sci. A. N. Kiselev, et al. It was decided to devote one of the forthcoming sessions of the Division of Chemical Science to the special problem of developing chemistry in light of the decisions of the May Plenum of the CC CPSU.

After this, scientific papers were read. Some interesting results were reported by V. I. Spitsyn in a paper on the "Effects of Radiation on the Physicochemical Properties of Solids." The author and his co-workers (I. E. Mikhailenko, V. G. Finikov, V. V. Gromov, et al.) studied the effects of radiation on the rates of isotopic exchange, adsorption, and other properties of solids. At high temperatures (840°) the rate of isotopic sulfur exchange between potassium sulfate (tagged with S^{35}) and gaseous sulfur trioxide depends on the specific activity of K_2SO_4. When the specific activity was increased from 0.01 to 2 mC/g the rate of isotopic exchange in the above described system increased by approximately 6 times. A further increase in the specific activity of K_2SO_4 to 10-20 mC/g decreased the rate of isotopic exchange.

Similar results were obtained in the investigation of the isotopic oxygen exchange in the $Na_2SO_4-O_2$ system at high temperatures (680-780°). Gaseous oxygen was tagged with O^{18} while the Na_2SO_4 sample contained various amounts of radioactive sulfur isotope S^{35}. The rate of isotopic exchange was measured by means of mass-spectrophotometry. When the specific activity of Na_2SO_4 was increased to 1 mC/g the exchange was accelerated, but a further increase slowed it down. A relation was detected between the amounts of dyes adsorbed on the barium sulfate precipitate and the S^{35} contents in the latter. A. A. Balandin, V. I. Spitsyn, N. P. Dobrosel'skaia, and I. E. Mikhailenko established that the rate of catalytic dehydration of cyclohexanol over $MgSO_4 + Na_2SO_4$ increased if more radioactive sulfur S^{35} was introduced. The observed effects were evidently related to the changes in the

*Central Committee of the Communist Party of the Soviet Union.

crystal lattice caused by radiation and the resulting increase in chemical activity on the surface of solids. The phenomena described can probably have various practical applications. The paper resulted in a lively discussion.

Corr. Member Acad. Sci. USSR V. M. Vdovenko reported on the: "Nitrates of Some Radioactive Elements and Their Distribution Between Two Immiscible Solvents." In modern radiochemistry, extraction, which is based on the distribution of radioelements between two immiscible solvents, is widely used for the separation of radioactive isotopes. One of the principal methods of separating radioisotopes involves the extraction of neutral inorganic complexes, often in the form of adducts, with organic solvents. The paper presented the results of a systematic investigation of the distribution of uranyl, neptunyl, and plutonyl nitrates and also gave the distribution behavior of other nitrates in aqueous and certain oxygen-containing organic solvents. The author was able to establish a series of interesting correlations of some practical importance, which related the effective salting-out action of nitrates not only to the nitrate ion concentration, but also to the properties of cations introduced into solution (radius, charge).

The experimental results obtained opened up the possibility of applying extraction methods to the isolation of of uranium and plutonium from aqueous solutions and of purifying them from fission products. Distribution behavior was investigated in the presence of calcium nitrate as the salting agent. By this process they were able to isolate 99% of plutonium formed in irradiated uranium, purify it from other activities by a factor of 80,000 (in comparison with the initial irradiated sample), and also separate 99% of uranium free of fission products (purified by a factor of a million).

Academician A. A. Balandin in a paper on the: "New Data on the Structural and Energy Relationships in Catalysis," noted that: "catalysis will be of paramount importance in the realization of the decisions of the May Plenum of the CC CPSU." After a brief survey of the contemporary state of catalysis, he went on to discuss the results of some research aimed at developing a Multiplet Theory of Catalysis. The Multiplet Theory has two aspects – structure and energy. The following results on the structural factors in catalysis were obtained from research carried out in 1956-57. Hydrogenation of complex molecules (such as could not be placed flat on a plane, for example triptycene and dianthrylenedibenzoquinone derivatives) on nickel showed that the active centers were located on protuberances topped by planes on which the reacting parts of molecules would lie down. The method used permits an estimation of the size of active centers.

A dehydrogenation study of twelve alcohols on an acid catalyst indicated that the reacting atoms in those molecules were oriented toward the catalyst. From the adsorption coefficients the changes in free energy, enthalpy, and entropy of adsorption were determined. A method of some practical importance was worked out for the preparation of isoprene from isopentene in high yields, and the kinetics of this reaction were investigated. It was found that at low temperatures the alcohol molecules are adsorbed parallel to the aluminum oxide surface, while at high temperatures perpendicularly. Similar results were obtained in the laboratory of A. V. Kiselev on carbon black. They investigated the dehydrogenation of cyclohexane on rhenium as predicted by the Multiplet theory. They found that the structural relationship between a catalyst and carrier is also important. Rhenium on carbon was the most active catalyst.

Concerning the work done in 1956-57 on the energy relationships, M. I. Temkin and N. I. Kabozev derived relationships similar to the ones derived from the Multiplet theory. The lecturer obtained more precise values for the the energies he had previously assigned to the bonds between nickel and organic compounds. The new data was applied to the calculation of reaction sequences in the hydrogenation of many polyfunctional compounds. A new variation of the Kinetic method of determining catalyst–compound bond energies was worked out; it was based on the Multiplet theory. In this manner the energies of various bonds to iron, palladium, and platinum were determined. These data provided an explanation for the correlations found by B. A. Kazanskii and co-workers in their study of opening and closing of hydrocarbon rings.

A particularly large amount of work has been devoted to the energy determinations of bonds with numerous oxide catalysts (in particular rare earths) and to the dehydrogenation of hydrocarbons and alcohols as well as dehydration of the latter. New catalysts were discovered, the dependence of bond energy on the chemical nature and source of the catalyst were determined, as well as dependence on the nature of the carrier. It was discovered that there was a considerable difference in the bond energies of dehydration catalysts and those with compound action. The results are in full accord with the Multiplet theory. The above mentioned papers permitted an extension of the Multiplet theory to fermentation and asymmetric catalysis.

Dr. Chem. Sci. B. M. Mikhailov delivered a paper on the subject of "Synthesis and Conversions of Organoboron Halides." Esters of organoboric acids react with phosphorus pentachloride to exchange alkoxy groups with chlorine. The reaction constitutes a general and simple method of preparing organoboron chlorides. Using this method one can convert esters of disubstituted boric acids to symmetric or unsymmetric dialkyl and diarylboron chlorides, and also to alkyl(aryl)boron chlorides. Depending on the ratio of reagents, esters of monosubstituted boric acids can be converted to either esters of alkyl(aryl)chloroboric acids or to alkyl(aryl)boron dichlorides. The paper also included results on the study of chemical properties of various types of organoboron chlorides which become readily available after a single method of preparing them was discovered. Their reactions with water, alcohols, organic acids and anhydrides, ammonia, and amines were investigated. It was established that conversions of organoboron chlorides proceed through an intermediate stage of complex formation and are often accompanied by symmetrization processes. The reactivity of chlorides strongly depends on the nature of organic radicals making up the chlorides and the reagents. During the investigation of the reactivity of chlorides many new types of organoboron compounds were prepared.

The lecture resulted in a very lively discussion, in which Corr. Member Acad. Sci. USSR A. D. Petrov, Acad. M. M. Shemiakin, Dr. Chem. Sci. K. M. Gorbunova, participated. They noted that organoboron compounds have already found important practical applications, and that research in this field can be not only of a theoretical but also of some practical interest.

SYMPOSIUM ON THE ORGANIC AND NONSILICATE CHEMISTRY OF SILICON. DRESDEN, MAY 12-14, 1958

The symposium on the organic and nonsilicate chemistry of silicon held in Dresden (May 12-14 of this year) was organized by the GDR* Chemical Society. A total of 28 papers were read and discussed at the symposium – 13 were delivered by GDR Chemists, 8 by Soviet Chemists, and 7 by West German Chemists. More than half the papers were devoted to research in the field of organic chemistry of silicon, the remaining ones were concerned with the nonsilicate chemistry of silicon, the analysis of organosilicon compounds. , and some special technological applications of organosilicon compounds. The symposium, which was held at the Botanical Institute of the Technical High School, attracted the attention not only of GDR scientists and technicians working in the field of silicon chemistry, but also specialists of other countries – USSR, Czechoslovak Peoples' Republic, and German Federal Republic. Besides the official delegation from the Academy of Sciences USSR (N. S. Nametkin – head of the delegation, M. G. Voronkov, A. A. Zhdanov, D. N. Andreev, and V. A. Ponomarenko) 24 other Soviet scientists and engineers working in the field of organosilicon chemistry participated in the symposium.

Of course, it is impossible to dwell even briefly in this report on all the papers delivered. We will only mention some of them. Half the papers delivered by the GDR chemists were contributed by the workers of the Chemical Institute of Silicones and Organic Fluorine Compounds in Radebeule. The remaining papers of the GDR Chemists represented some of the trends in the research on organic and nonsilicate silicon chemistry conducted at the universities in Halle, Iena, Rostock, and Dresden.

One of the longest papers delivered by the GDR organosilicon chemists was that of R. Müller, the director of the Institute of Silicone Chemistry in Radebeule. The paper was of a theoretical nature, and in it R. Müller gave a historical survey of the development of organic and inorganic silicon chemistry from two points of view, its similarity and dissimilarity to carbon chemistry. Applying concepts which involved the use of 3d silicon orbitals in the formation of complexes, R. Müller tried to explain from a single point of view the mechanisms of such reactions of organosilicon compounds as alkaline hydrolysis, fluorination, polymerization, acid hydrolysis, etc.

G. Kriegsmann delivered a detailed paper devoted to the problem of atomic interactions detected in the vibrational spectra (Raman and Infrared). A study of interatomic distances and force constants of a series of

*German Democratic Republic.

organosilicon compounds enabled the author to confirm the previously noted increased interaction between silicon and its bonds with electronegative elements. These particular properties of bonds between electronegative elements and silicon are, in the opinion of the author, connected with the tendency to fill the vacant 3d orbitals in the latter.

We would also like to mention two more papers delivered by the GDR organosilicon chemists, S. Munkelt and G. Beyer. S. Munkelt's paper dealt with the synthesis of alkenylsilanes by dehydrochlorination of chloroalkyl silanes over ferrosilicon at elevated temperatures. Munkelt worked out a continuous process for the preparation of alkenylsilanes (vinyltrichlorosilane, allytrichlorosilane, and others) by this reaction. G. Beyer's paper was devoted to an extremely detailed investigation of a reaction between carbon tetrachloride and silicon at 200-400°. The author of this paper succeeded in determining the optimum conditions for carrying out this reaction (~310°); these give the maximum yield of products from a direct reaction in which are formed Si—C bonds and relatively small amounts of silicon tetrachloride. Among the reaction products there were compounds of the type: $Cl_3SiC{\equiv}CSiCl_3$, $Cl_3SiC(Cl)=C(Cl)SiCl_3$ and $(Cl_3Si)_4C$. The following reaction mechanism was proposed:

$$Cl_4C \rightarrow Cl_3CCCl_3 \rightarrow Cl_2C=CCl_2 \xrightarrow{Si} Cl_3SiC(Cl)=C(Cl)SiCl_3$$
$$Cl_2C=CCl_2 \xrightarrow{Si} ClC{\equiv}CCl \rightarrow Cl_3SiC{\equiv}CSiCl_3$$

The papers of G. Schott, F. Runge, G. Wessel, G. Reuter, R. Kene, H. Date, G. Becherer, and O. Düring, which showed the development of research in the field of theoretical and applied silicon chemistry in GDR, were actively discussed at the symposium.

The papers of Soviet organosilicon chemists were read on the second and third day of the symposium. Before our papers were delivered, the head of the Soviet delegation, Dr. Chem. Sci. N. S. Nametkin, made a short introductory speech in which he thanked, in the name of all the participating Soviet chemists and engineers, the German Chemical Society and the director of the Symposium, Prof. R. Müller, for the invitation to the symposium and delivered to the German Chemists working in the field of organic and inorganic silicon chemistry sincere greetings from Soviet silicon chemists. In answer to this Prof. R. Müller noted the advantages derived from having Soviet organosilicon chemists participate in the symposium. Papers delivered at the symposium were from a series of Soviet laboratories engated in silicon work (K. A. Andrianov's, B. N. Dolgov's, A. D. Petrov's and A. V. Topchiev's).

In the name of K. A. Andrianov and his own, A. A. Zhdanov (Institute of Heteroorganic Compounds) delivered two papers dealing with the synthesis of polyorganometalsiloxanes containing Al, Ti, P, and other metals.

Both of these two papers as well as others delivered by our delegation, aroused a great interest among the listeners. Soviet chemists are fairly well acquainted with these parts of K. A. Andrianov's research, which he has extensively developed in recent years. A paper by N. S. Leznov, L. A. Sabun, and K. A. Andrianov contained some interesting results on the action of various organic and inorganic acids and aldehydes on diethyldiethoxysilane and on its mixture with triethylethoxysilane which lead to the formation of polydiethylsiloxane liquids. The paper was delivered by N. S. Leznov. D. N. Andreev (Institute of Silicate Chemistry, Leningrad) discussed the action of silent electric discharge on CH_3SiCl_3 and $(CH_3)_2SiCl_2$. The condensation products formed in this reaction, $Cl_3SiCH_2SiCl_2CH_2SiCl_3$, $Cl_3SiCH_2CH_2SiCl_2CH_2SiCl_3$, $CH_3SiCl_2CH_2SiCl_2CH_3$, et al., were very thoroughly studied in this work. The results obtained could be easily explained if a free radicals chain reaction mechanism was assumed.

A detailed paper by M. G. Voronkov (Institute of Silicate Chemistry, Leningrad) was devoted to the development of two new synthetic methods for the preparation of various alkylalkoxysilanes and siloxanes by the cleavage of linear and cyclic polysiloxanes with alkoxy and halosilanes in the presence of nucleophilic (KOH et al.) and electrophilic ($FeCl_3$) reagents. M. G. Voronkov's paper contained a detailed analysis of the mechanism of these two reactions. A paper by A. V. Topchiev, N. S. Nametkin, T. I. Chernysheva and S. G. Durgar'ian (Petroleum Institute Acad. Sci. USSR, Moscow) presented some new results from the research on additions of various alkyl, aryl and chlorosilanes to allyl and diallylsilanes, allylhydroxysilanes, allyl alcohol, dimethylvinylcarbinol, and other tertiary alcohols. Benzoyl peroxide and platinum on carbon were used as catalysts. The paper was delivered by N. S. Nametkin.

The Institute of Organic Chemistry (Moscow) contributed two papers to the symposium. Work on the synthesis and properties of various acetylene and diene organosilicon compounds was discussed in a paper by A. D. Petrov, S. I. Sadykh-Zade, and L. L. Shchukovskaia. V. A. Ponomarenko reported at the symposium on the synthesis of a series of fluorinated organosilicon monomers: $CH_3SiCl_2CF_2CF_2H$, $CH_3SiCl_2CF_2CFClH$, $CH_3SiCl_2CH_2CF_2H$, $RSiCl_2CH_2CH_2OCF_2CF_2H$, $RSiCl_2CH_2CH_2CH_2OCF_2CFClH$, and others by the addition of silicon hydrides to unsaturated compounds containing fluorine, in the presence of Pt on carbon, Pt on SiO_2, and H_2PtCl_6 as catalysts.

Of the papers delivered by West-German Chemists one should mention those by F. Chenglein, G. Kohlschütter, G. Fritz, and U. Wannagat. F. Chenglein's paper (Carlsruhe) discussed some methods developed for the synthesis of polysiloxanes containing $O-CH_2-O$, $O-CH(CCl_3)_3$ groups in their chains as well as B, P, N, As, Pb, Sn, Sb, and other elements. Essentially Chenglein investigated the reactions of alkyl and arylchlorosilanes with organic hydroxyl compounds and their derivatives, such as: methyleneglycol diacetate, chloral, terephthalic acid, resorcinol, pyrocathecol, gallic acid, amino acids, hydroxylamine, and other similar organic compounds. As F. Chenglein declared himself, that the polymers obtained had no practical value; the sole purpose of his investigation was to work out synthetic methods for new modified polysiloxanes. In G. Kohlschütter's work (Darmstadt) alkylchlorosilanes were used to study some problems connected with the composition of compounds in a silica gel–water system. Thus, when silica gel was treated with $(CH_3)_3SiCl$ organosilicon compounds were formed on the surface. By means of analytical methods this reaction was studied very thoroughly. The results obtained are important in the solution of problems connected with water absorption on silica gel.

Two papers by U. Wannagat (Aachen) dealt with inorganic compounds of silicon. Thus, in the first paper the author presented some experimental results on the synthesis and properties of a series of organosilicon derivatives of hydrazine. In the second paper U. Wannagat presented the results from an investigation of various adducts between halosilanes and N-heterocyclic compounds–pyridine, α-picoline, collidine, quinoline, 8-hydroxyquinoline, et al. The following adducts were obtained: $SiF_4 \cdot 2Py$, $SiCl_4 \cdot 2Py$, $HSiCl_3 \cdot 2Py$, $SiBr_4 \cdot 2Py$, $SiI_4 \cdot 4Py$, $Si_2Cl_6 \cdot 3Py$, $Si_3Cl_8 \cdot \cdot 2Py$, et al. At the same the reactions of these adducts with H_2O, CH_3OH, H_2S, SO_2, SO_3, and HCl were also investigated. The question as to the structure of these adducts may be of some use in helping explain the nature of chemical bonds between silicon and other elements and in the study of specific reactivity of inorganic as well as organic silicon compounds.

G. Fritz (Münster) reported on the reaction between silanes and ethylene, as well as on the thermal decomposition of alkylsilanes and chloroalkylsilanes.

The symposium in Dresden showed that both in the German Democratic Republic as well as in Western Germany there has been in recent years an increased activity over a wide range of theoretical, synthetic, and applied problems in the field of organic and inorganic chemistry of silicon. Despite the overloaded program the symposium went on smoothly and was of immense benefit to all the participants.

At the conclusion of the symposium, the guests from USSR and Czechoslovak Peoples Republic were given the opportunity to get acquainted with the Institute of Silicones and Fluoroorganic Compounds in Radebeule, and also with the industrial production of silicones in Nünchritz. The Institute of Silicones and Fluoroorganic Compounds is primarily concerned with finding new methods of preparing and technically applying silico- and fluoroorganic compounds to various branches of technology and industry. The Institute employs about 210 scientists, engineers, laboratory assistants, workers, and maintenance staff. A typical job for all the laboratories in the Institute is the solution of practical problems (direct synthesis of silicone oils, silicone rubbers, silicone resins and varnishes) which arise in laboratories of fluoroorganic compounds, test stations, analytical labs, and labs for testing the physical and physicochemical properties of polymers. Thanks to the work done at the Institute, the GDR (Nünchritz) is now actually able to manufacture silicones – direct synthesis of methylchlorosilanes, manufacture of methylphenylsilicone varnishes, oils, greases, antifoaming and hydrophobic agents.

They intend to enlarge considerably in the coming years the manufacture of organosilicon products. With this in mind the Institute of Silicones and Fluoroorganic Compounds in Radebeule as well as the industrial production of silicones in Nünchritz will be enlarged. Departing from the German Democratic Republic we were convinced that the new problems facing the organosilicon industry in the GDR will be solved successfully.

V. A. Ponomarenko

PHYSICS and HEAT TECHNOLOGY of REACTORS

Supplement No. 1 –
– 1958 –
SOVIET JOURNAL OF ATOMIC ENERGY

- nineteen original papers by leading Soviet authorities
- translated from Russian, 178 pages, profusely illustrated
- publication: October, 1958

The papers in this important volume may conveniently be divided into two sections: The first deals mainly with reactor physics – calculations; specialized experiments; reactor safety; and a variety of related problems. (These papers will be of special value to the Western scientist, because they encompass a wide circle of problems which have not been studied or treated in the literature to any great extent.)

The second group is more concerned with engineering aspects: heat problems that arise in power reactors; obtaining the highest efficiency of heat removal and the greatest utilization of the heat generated in the core of the reactor. The intimately related subject of radioactive loading of the reactor heat removal systems is also considered at length.

Cloth-Bound $22.50

C/b CONSULTANTS BUREAU, INC.
227 W. 17th St., NEW YORK 11, N.Y.

recent Russian research

—in complete English translation

A New Method in the Theory of SUPERCONDUCTIVITY

BY N. N. BOGOLIUBOV
V. V. TOLMACHEV
AND D. V. SHIRKOV

IN THIS unprecedented *complete* solution to the perplexing problem of constructing a microscopic theory of superconductivity, the authors explain their new method—*a result of the research of N. N. Bogoliubov and V. V. Tolmachev*—based on a physical and mathematical analogy with superfluidity.

Here they give *calculations for the energy of the superconducting ground state using Fröhlich's Hamiltonian, as well as of the one-fermion and collective elementary excited states;* they provide a detailed analysis of *the role of the Coulomb interaction between the electrons in the theory of superconductivity;* and demonstrate how *a system of fermions is treated with a fourth-order interaction Hamiltonian and establish the criterion for its superconductivity* — all of which is indicated in greater detail in the complete table of contents shown to the right.

cloth bound • 130 pages • $5.75

Complete Table of Contents

INTRODUCTION

outline of the present state of superconductivity theory • brief description of the microscopic theory of superconductivity

FRÖHLICH'S MODEL OF SUPERCONDUCTIVITY

principle of compensation of "dangerous" diagrams • analysis of the compensation equation • the ground state and the one-fermion excited states

RENORMALIZED THEORY OF SUPERCONDUCTIVITY IN FRÖHLICH'S MODEL

compensation and renormalization equations • simplification of the relations obtained • energy difference between normal and superconducting states • the property of superconductivity

SPECTRUM OF COLLECTIVE EXCITATIONS IN THE SUPERCONDUCTING STATE

the method of approximate second quantization as applied to a system with Coulomb interaction • collective excitations in Fröhlich's model • solution of the secular equations—longitudinal excitations • solution of the secular equations—transverse excitations

INCLUSION OF THE COULOMB INTERACTION BETWEEN ELECTRONS

statement of the problem • compensation and renormalization conditions • transition to the "time-dependent" formalism • final form of the compensation equation for the electron diagrams • energies of the ground state of the one-fermion excited state • transformation of the $Q(k, k')$ kernel • finding λ, μ, and $\tilde{\omega}$ • a related model

QUALITATIVE DESCRIPTION OF EFFECTS DUE TO THE COULOMB INTERACTION

approximate determination of the renormalized $\tilde{\omega}$ and g • the properties of Q_c and Q_{ph} • general properties of the basic compensation equation

FERMI SYSTEMS WITH WEAK INTERACTION

formulation of the BCS theory • compensation equations • collective excitations — influence of the Coulomb interaction

CONCLUSION

the thermodynamics and electrodynamics of the superconducting state • a qualitative picture of the phenomenon of superconductivity

APPENDICES

on the question of superfluidity in nuclear matter • on a variational principle in the many-body problem

CB translations by bilingual scientists include all diagrammatic, photographic and tabular material integral with the text.

(c/b)

CONSULTANTS BUREAU, INC.

227 WEST 17TH STREET, NEW YORK 11, N. Y.